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Field Evaluation of Long-Term Performance and Use of Biosand Filters in Posoltega, Nicaragua

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An evaluation was conducted in 2007 on biosand filters that were installed in Posoltega, Nicaragua in 1999 and 2004. The objectives were to characterize the condition and use of filters eight and three years after installation, determine filter performance of those filters still in use, and identify determinants of successful long-term use and performance. Methods consisted of household identification, user questionnaires, and water quality testing. Of the 234 filters installed, only 24 were found to still be in use. Average log reductions were 1.73 (98%) for total coliforms, 1.36 (96%) for *Escherichia Coli*, and 0.91 (88%) for turbidity. Statistically significant effects were detected for the magnitude of the contamination of source water, the peak hydraulic loading rate, and the standing depth of water over the filter media. Questionnaire results indicated user training on filter maintenance could improve the peak hydraulic loading rate and hence filter performance. The low rate of sustained use (10%) is an indication of failed implementation, and is attributable to structural failure, particularly cracking of the concrete filters from 2004. Nonetheless, this evaluation demonstrated the biosand filter technology to be robust since those filters still in use were performing as expected three and eight years postimplementation.

Key words: **biosand filter, household water treatment, point of use, developing countries, Nicaragua**

Introduction

Access to clean water, free of pathogens and other contaminants, is essential for human life and vital for the development of healthy communities. Nonetheless, there are 1.1 billion people worldwide without access to safe drinking water, and there are 1.6 million deaths every year attributable to the lack of access to safe drinking water and basic sanitation; 90% of these deaths are among children under the age of five (WHO 2005). The majority of these cases are in rural areas of developing countries, where centralized distribution systems do not exist or are unable to provide clean water to the community. A novel approach that has been forwarded by the World Health Organization (WHO) and other water, sanitation, and health policy makers worldwide is Household Water Treatment, where a family takes responsibility for treating their own drinking water through the application of a household-based technology. Dr. Jamie Bartram, Coordinator for the Water, Sanitation, and Health Programme of the WHO, states that "there is now conclusive evidence that simple, acceptable, low cost interventions at the household and community levels are capable of dramatically reducing the risks of diarrheal disease and death. These household interventions are cost-effective, with an overall benefit of up to 60 US$ per 1 US$ invested" (Sobsey 2002, forward).

One type of household water treatment technology is the biosand filter, which is an intermittently-operated, small-scale slow-sand filter. The biosand filter consists of a housing structure (typically concrete or plastic) that contains a column of approximately 0.5 m of fine sand. The sand is underlain by a granular underdrain and an outlet pipe which rises up the wall of the structure to discharge at a point higher than the sand column, thus maintaining a standing depth of water in the filter, and the media in an aqueous environment. The biosand filter is used by charging the top of the filter with a bucket of water, and collecting the filtered water from the outlet pipe. A diffuser plate above the standing water depth disperses the flow and reduces impact on the biological layer (discussed below), which is important for water treatment. The low construction and installation costs, ease of use, minimal maintenance requirements, and simple self-contained design make it an appropriate technology for application in remote and rural locations of developing countries. The earliest biosand filters were introduced in the Nandaime Valley of Nicaragua as a pilot project in 1993 (Manz et al. 1993). The technology has since spread to more than 140,000 households across 38 countries (S. Kaczmer, Centre for Affordable Water and Sanitation Technology, personal communication, February 1, 2008).

A traditional slow-sand filter relies on a naturally occurring biological layer, or *schmutzdecke*, within the top depth of sand to treat contaminated water. Influent waterborne pathogens that pass through this layer are removed through "inactivation (degradation and/or predation), physical straining, and attachment to the sand grains" (Dullemont et al. 2006). A traditional slow-sand

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filter can remove between 1 and 3 log units of coliform bacteria (Amy et al. 2006), between 2 and 4 log units of enteric viruses (Amy et al. 2006), and up to 4 log units of *Giardia* cysts and *Cryptosporidium* oocysts (Amy et al. 2006). As an intermittently operated slow-sand filter, the biosand filter also relies on the biological layer at the top of the sand for the removal of influent waterborne pathogens. Laboratory evaluations of the biosand filter have demonstrated its ability to consistently remove up to 2 log units of faecal coliforms (Buzunis 1995) and *Escherichia coli* (Stauber et al. 2006), and up to 4 log units of *Giardia* cysts and *Cryptosporidium* oocysts (Palmateer et al. 1999). Another laboratory evaluation found geometric mean reductions of 1.9 log units for *E. coli* and 2.1 log units for echovirus 12 (Elliott et al. 2008). These evaluations indicate that in the laboratory setting, the efficiency of pathogen removal by the biosand filter is consistent with that of a traditional slow-sand filter.

Pathogen removal by the biosand filter has also been evaluated in a number of field studies (Table 1). The majority of these studies were field reports from implementing organizations that undertook limited water quality testing on recently installed filters to demonstrate the short-term success of this technology; these field reports did not typically undergo any peer review process. It is only within recent years that peer-reviewed papers have been published on the long-term efficacy of biosand filters installed in homes and communities (Stauber et al. 2009; Duke et al. 2006).

A randomized controlled trial was recently conducted in Bonao, Dominican Republic to document the reduction in diarrheal disease following biosand filter intervention. The results indicate households that received filters exhibited a 47% reduction in diarrheal disease compared with control households, "indicating a significant effect of the [biosand filter] against waterborne diarrheal disease" (Stauber et al. 2009). Before the intervention, water quality sampling indicated geometric mean concentrations of *E. coli* in the source water of 22 and 21 MPN/100 mL (MPN = most probable number) for intervention and control households respectively; following the intervention, households that received biosand filters exhibited an average reduction of 48% in drinking water concentrations of *E. coli* over the course of the six-month study period (Stauber et al. 2009).

To provide further evidence on the long-term efficacy of the biosand filter as an intervention for improving drinking water quality, an evaluation was conducted in 2007 on biosand filters that were installed in 1999 and 2004 in Posoltega, Nicaragua. The objectives of the study were to:

- Characterize the physical condition and operation of the biosand filters eight years and three years after implementation (i.e., post-1999 and -2004, respectively);
- Determine the performance (measured as coliform and turbidity removal efficiency) of the biosand filters still in operation;
- Identify the determinants of long-term performance and use of the biosand filters in Posoltega, Nicaragua.

Baughen et al. (1999) undertook a field study at the same location during the initial introduction of the filters to Posoltega in 1999; the availability of this data provided an additional point of reference in evaluating the filter performance.

TABLE 1. Summary of previous field evaluations of the biosand filter

Reference	*Organization* [a]	*Country*	*Time since installation*	*Indicator organism*	*Removal rate*
Manz et al. (1993)	University of Calgary	Nicaragua	3 to 8 weeks	Fecal coliform	99%
Buzunis (1995)	University of Calgary	Nicaragua	3 weeks	Fecal coliform	97%
Baughen et al. (1999)	University of Calgary	Nicaragua	1 month	Fecal coliform	80%
Mol (2001)	Medair	Kenya	3 weeks	Fecal coliform	93%
Dies et al. (2003)	Clean Water for Nepal	Nepal	"Recently"	*E. coli*	95%
Bojcevska & Jergil (2003)	Uppsala University	Mozambique	1 month	Cyanobacteria	96%
Fewster et al. (2004)	Bushproof – Medair	Kenya	2.5 to 4 years	Fecal coliform	70% <10 cfu/100mL
Stauber et al. (2006)	University of North Carolina – Chapel Hill	Dominican Republic	1 year	*E. coli*	94%
Duke et al. (2006)	University of Victoria; CAWST	Haiti	5 years	*E. coli*	98.5%
Earwaker (2006)	Cranfield University – Silsoe	Ethiopa	5 to 7 years	*E. coli*	88%

[a] CAWST = Centre for Affordable Water and Sanitation Technology.

Setting

The rural communities of the Municipality of Posoltega have limited infrastructure. Communal drinking water systems are not available, and families rely on individual shallow wells for their source water. Previous studies have shown these wells are contaminated with pathogens and pesticides (CIRA 1999a, 1999b).

In October of 1998, this region was ravaged by Hurricane Mitch. Widespread flooding and a landslide resulted in two buried villages and approximately 2,500 deaths. In 1999, a nongovernmental organization (NGO) taking part in the relief effort following Hurricane Mitch manufactured biosand filters at their facility in Managua, Nicaragua and delivered them to 34 families in the community of El Trianón (Baughen et al. 1999). Approximately half of these filters were plastic structures, and half were concrete. In 2004, the same NGO returned to Posoltega to aid in the construction and deployment of 200 more concrete filters. These filters were built by community members at the local health center in Posoltega for the purpose of replacing defective filters in El Trianón and delivering new filters to households in the communities of San Gilberto, Posolteguilla, Buenos Aires, El Mojón, and San Agustín. A map of Posoltega identifying the communities that received biosand filters is shown in Fig. 1. Schematics of the concrete filters and plastic filters installed in these communities are included in Fig. 2.

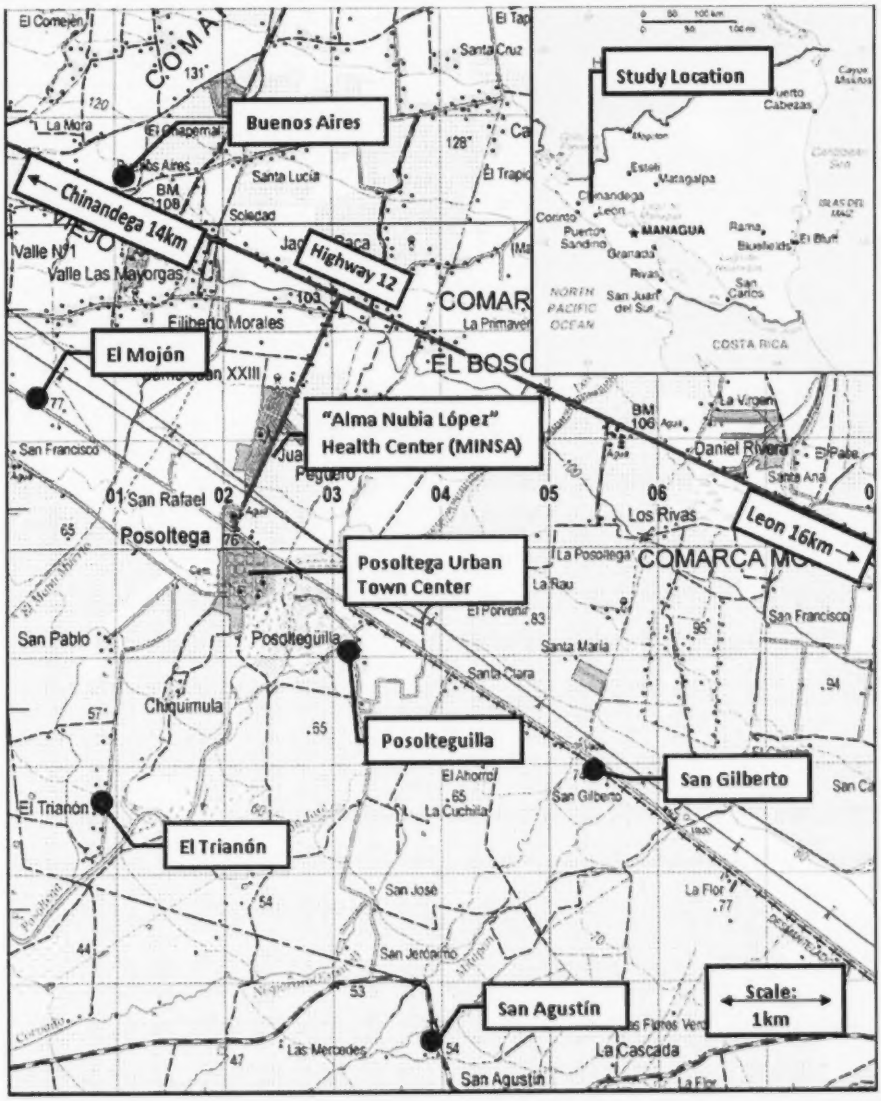

Fig. 1. Map of Posoltega and study communities. Sources: U.S. Department of State (2007) & INETER (2006).

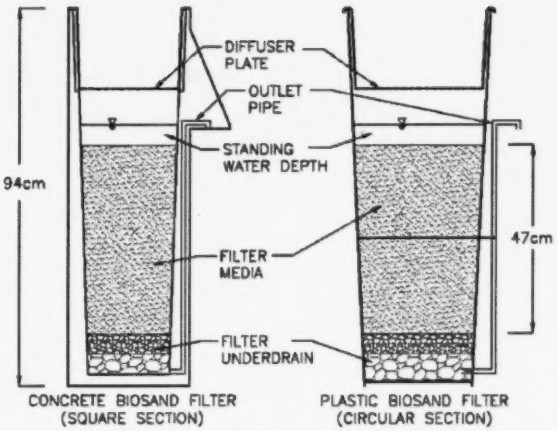

Fig. 2. Schematic of biosand filters installed in Posoltega.

Materials and Methods

The field investigation, conducted from January to April 2007, began with a systematic identification of the households where biosand filters had been installed, and where these filters were still in use. All filters that were found to be in use were inspected for their physical characteristics, and water quality testing was conducted on the source water and filtered water to determine filter performance. Household members were interviewed regarding the use and operation of the biosand filter, as well as other water and sanitation practices.

Household Identification

Researchers from the University of British Columbia and support staff from the local health centre visited the six communities (Posoltega, San Gilberto, Posolteguilla, Buenos Aires, El Mojón, and San Agustín) where filters were installed to identify those that were still in use. In El Trianón, every household in the community was visited to identify working filters and determine the failure mechanism in defective filters. In the communities of San Gilberto, Posolteguilla, Buenos Aires, and El Mojón, the high failure rate of the filters meant that houses with working filters were common knowledge and easily identified through communication with community members. In addition, approximately half of all households in these four communities that had received filters were visited to determine the failure mechanisms of those filters not in use. In San Agustín, a meeting with the community leader revealed that not a single filter was still in use on account of failure of the structure. Throughout the entire Municipality of Posoltega, biosand filters were being used in 24 households.

All 24 households with working filters were included in the filter evaluation component of the study. Nine of these households were selected for two more follow-up visits (a total of three visits each) to conduct additional water quality testing. The purpose of further testing was to provide a level of confidence in the results and estimate the variability in the results over the time period between visits. These nine households were selected to provide balanced representation of the different filter types (plastic or concrete), implementation years (1999 or 2004), communities, and water quality results encountered during the initial visits.

Household members consented to participate in two steps. During the initial visit, household members verbally consented to a visit by a study team member at a later date for data collection. During the second visit, household members gave their consent again, as evidenced by their actions in responding to the questionnaire. The University of British Columbia Behavioural Research Ethics Board approved the study.

Biosand Filter Inspection

The inspection process for biosand filters consisted of recording the location, implementation year, and structural material (concrete or plastic), checking the integrity of the structure for cracks and leaks, and ensuring the diffuser plate and lid were in place. The standing depth of water over the sand during the pause period between filter charges when there is no influent water was indicated by Buzunis (1995) to be an important operational parameter of the biosand filter. Diffusion of oxygen through this standing water depth is thought to keep aerobic organisms in the biological layer alive. The flow rate (hydraulic loading rate) has been found to be an important operational parameter for both traditional slow-sand filters (Hendricks and Bellamy 1991) and biosand filters (Buzunis 1995; Duke et al. 2006).

Standing water depth was measured before charging the filter with water. The flow rate through the filter was measured by recording the time to fill a 250-mL cup with water from the filter outlet after charging the top reservoir of the filter with a 20-L bucket of source water. The biosand filter operates under a falling head regime, and therefore this measurement was taken immediately after charging the filter so as to record the peak flow rate (which decreases with the falling head) and to ensure consistent measurement technique between filters. The volumetric flow rate was then normalized by the cross-sectional area, approximately 0.058 m^2 (24 by 24 cm) for the concrete filters and 0.086 m^2 (33-cm diameter) for the plastic filters, to yield the peak hydraulic loading rate in m^3/m^2/hour.

Questionnaire and Observational Data

A questionnaire was administered by the research team at each household, typically to the female head of household. The interview was conducted in Spanish and consisted of 43 questions covering family demographic information, water use, operation of the biosand filter,

and sanitation practices within the home. Filter users were also asked about training and any follow-up received from the implementing organization. Additional observational data was also recorded on the construction materials and layout of houses, condition of wells and latrines, and general level of hygiene.

Interview questions that related to filter operation included estimation of the total filtered volume per day (daily loading rate), filter sharing practices between families, frequency of filter maintenance, length of time since the last filter maintenance, and use of any other treatment methods.

Water Quality Testing

The evaluation of filter performance was based on removal of microbial indicator organisms and turbidity. The indicator organisms selected for this study were total coliforms and *E. coli*. While abundant in the intestine of warm-blooded mammals, *E. coli* is not typically able to thrive outside of the host. This organism is therefore used as an indicator of recent fecal contamination, and potentially fecal-derived pathogenic organisms (Feng et al. 2002). The WHO explicitly states that *E. coli* "should not be present in drinking-water" (WHO 2006); testing for *E. coli* allows for comparison to this standard.

Samples of the water were taken before it was introduced into the top of the filter (source water), and immediately after it had left the spout of the filter (filtered water). To evaluate the entire delivery system in its ability to provide clean drinking water, a third sample was taken from the stored filtered water currently being used as the family's source of drinking water (discussed in Vanderzwaag [2008]).

Standard Method 9222: Membrane Filter Technique for Members of the Coliform Group (APHA et al. 2005) was used for the enumeration of coliform bacteria in the sample water. Membrane filtration was conducted in the field using Potatest WE10005 (Wagtech International, Berkshire, U.K.). Field sterilization of the equipment was achieved through the combustion of methanol as per the manufacturer's operation manual (Wagtech International [no date]). The growth media m-coliBlue24 (Hach Company, Loveland, Colo.) was selected for this study for the simultaneous detection and differentiation of total coliforms and *E. coli*. The differential media contains enzymes which cause coliforms to produce red colonies by their ability to reduce TTC (2,3,5-triphenyltetrazolium chloride), and *E. coli* to produce blue colonies by their ability to hydrolyze the enzyme substrate BCIG (5-bromo-4-chloro-3-indolyl-beta-D-glucuronide) to an insoluble salt, while suppressing the growth of noncoliform organisms (Hach Company 1999).

Preliminary testing of the source water revealed such high levels of microbial contamination that the number of organisms in a 100-mL sample would have been too concentrated to produce evaluable results. Furthermore, the preliminary testing suggested significant variation in organism concentrations, thus testing sample volumes differing by an order of magnitude would improve the likelihood of achieving evaluable results for both indicator organisms versus testing a single sample volume. In light of this, sample volumes of 1 and 10 mL were taken of the source water, and sample volumes of 10 and 100 mL were taken of the filtered water. The 1-mL samples were measured using sterile, single-use pipettes; the 10-mL samples were measured using sterilized glass beakers; and the 100-mL samples were measured by filling the reservoir tube on the membrane filtration equipment to the appropriate indicated mark.

The prepared specimens were transported to the local health center in Posoltega where they were incubated at 35°C for 24 hours. After the incubation period the colonies were enumerated with the assistance of a 5× magnification handheld lens and a tally counter. Concentrations below detection limits were recorded as 0.5. The results were factored according to the sample volume, and reported as CFU per 100 mL. Where both the small and large sample volumes yielded enumerable results, the plate count within or closest to the range of 15 to 150 CFU was selected, and a coefficient of variation between the two results was computed. This approach is discussed further and evaluated in Vanderzwaag et al. (2009). A digital photograph was also taken of each series for record keeping. Two blank samples per day were taken for quality control, representing 11% of all samples.

The turbidity meter Wag-WT3020 (Wagtech International, Berkshire, U.K.) was used to measure turbidity, in nephelometric turbidity units (NTU), of the water samples in the field. At least five readings were recorded for every sample, and the geometric mean of these readings was reported and used for subsequent analysis. This instrument was calibrated every day using the supplied control vials.

Statistical Methods

The filtration efficiency was calculated as the log-reduction (LR) between the paired source and filtered water quality results from the household visit. For the nine households that were visited three times, the arithmetic mean LR was computed from the three visits and used as a single data point in subsequent reporting and analysis. Student's *t*-test (two-tailed heteroscedastic) was used to test the statistical significance of the differences in means of two data sets, and the statistical significance of correlations. The Shapiro-Wilk test was used to test if a particular data set was consistent with a normal or log-normal distribution. Arithmetic means and standard deviations (SD) were reported for data sets consistent with a normal distribution, whereas geometric means and geometric standard deviations (GSD) were reported for data sets consistent with log-normal distributions.

Results and Discussion

Of the 234 biosand filters installed in Posoltega, Nicaragua during the 1999 and 2004 implementation programs, 24 filters were found to still be in operation in 2007. This is a rate of sustained use of 10%.

Water Quality Results

The water quality results for microbial and turbidity contamination varied over several orders of magnitude within each series for source and filtered water, and the distribution of each series was found to be consistent with a log-normal distribution by the Shapiro-Wilk test (W = 0.94 to 0.97, α = 0.05), hence geometric means and the respective geometric standard deviations (GSDs) are reported. Geometric mean source water concentrations were 13,000 CFU/100 mL (GSD = 3.9) for total coliforms, 130 CFU/100 mL (GSD = 8.9) for *E. coli*, and 1.5 NTU (GSD = 2.8) for turbidity. Geometric mean filtered water concentrations were 250 CFU/100 mL (GSD = 4.9) for total coliforms, 6 CFU/100 mL (GSD = 5.6) for *E. coli*, and 0.19 NTU (GSD = 2.6) for turbidity. These results are displayed in Fig. 3.

The field methodology of testing duplicate water samples at different volumes yielded 179 pairs of tests (358 results) where both the larger and smaller sample volumes yielded countable, useable results: 104 pairs for *E. coli* and 75 pairs for total coliforms. The average coefficient of variation computed between the results from the corresponding pairs of larger and smaller volumes was 51% (SD = 35%). Further discussion can be found in Vanderzwaag et al. (2009).

Filter Performance

The distribution of LR values was found to be consistent with a normal distribution by the Shapiro-Wilk test (W = 0.955 to 0.97, α = 0.05), and therefore arithmetic means and the respective standard deviations (SD) of LR are reported. The mean LR was found to be 1.73 (SD = 1.05) for total coliforms, 1.36 (SD = 0.82) for *E. coli*, and 0.91 (SD = 0.63) for turbidity. The equivalent percent removal was 98% for total coliforms and 96% for *E. coli*. The equivalent percent removal was 88% for turbidity. Given that the source water turbidity was generally quite good with 48% reporting below 1.0 NTU and 67% reporting below 3.0 NTU, the expectation is that the biosand filter would be at least as effective in terms of turbidity removal for more turbid source water.

Out of a total of 72 LR values, five were negative, representing cases where filtered water exhibited higher concentrations than the source water. With one exception, negative LR values were bounded by approximately -0.3, representing a factor of 2.0 between the source and filtered water. The coefficient of variation between any two numbers that differ by a factor of 2.0 is 47%, which is within range of the coefficient of variation calculated above for the water quality testing methods. Those filters

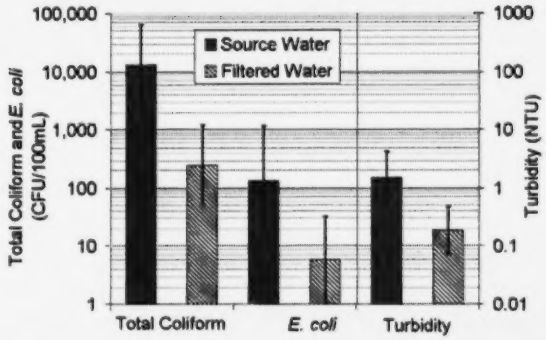

Fig. 3. Source and filtered water quality results. Error bars indicate one geometric standard deviation.

with poor filtration performance may therefore yield negative LR values as a result of the confidence intervals around the observed data points. These observations may also have resulted from biological processes within the filter itself, such as detachment, sloughing, or breakthrough, as discussed in Dullemont et al (2006). The negative LR values did, however, correlate well with the linear models of determinants of filter performance discussed below.

The mean LR values of 1.73 (i.e., 98% removal) for total coliforms and 1.36 (i.e., 96% removal) for *E. coli* are within the expected performance range of a traditional slow-sand filter. These values are also within the expected performance range when compared with laboratory studies of the biosand filter (Palmateer et al. 1999; Stauber 2006), and with other field studies of the biosand filter (presented in Table 1). The results of this study found the filters to perform with greater efficiency than originally reported by Baughen et al. (1999) in the evaluation of the filters installed in 1999 (80%). This is likely due to the fact that the original evaluation was undertaken while the biological layer was still ripening in the recently-installed filters.

Evidence from this evaluation and the other studies in Table 1 suggests that the biosand filter technology is robust. Provided that the structural elements remain sound, biosand filters will continue to perform within the expected range of new (ripened) filters, even up to eight years after implementation.

Stauber et al. (2009) reported a reduction in the geometric mean drinking water concentration of *E. coli* by 48% from 21 to 11 MPN/100 mL, and a corresponding reduction by 47% in the incidence of diarrheal disease among households that used the biosand filter compared with control households. The improvements in water quality achieved by the biosand filters in the study in Posoltega were significantly greater, with geometric mean drinking water concentrations of *E. coli* reduced by 96% from 130 to 6 CFU/100 mL.

Nevertheless, the filtered water in this study does not for the most part meet the WHO guidelines for drinking water quality, which states that *E. coli* or thermotolerant

coliform bacteria must not be detectable in any 100-mL sample (i.e., 0 CFU/100 mL) of water directly intended for drinking (WHO 2006). Of the 24 filters tested, three (13%) yielded filtered water quality results of <1 CFU/100 mL *E. coli*, and 16 (67%) yielded results of <10 CFU/100 mL *E. coli*. This indicates that the biosand filters alone were not sufficient to provide clean water in this situation in the absence of additional treatment such as disinfection.

Determinants of Filter Performance

The performance of the biosand filters (measured as LR of total coliforms, *E. coli*, and turbidity across the filter) was found to correlate with the operational variables of source water contamination, hydraulic loading rate, and standing water depth, as discussed below. Given the many physical, biological, and chemical factors that affect filter performance for slow-sand filters (see Hendricks and Bellamy 1991; Pyper and Logsdon 1991; Dullemont et al. 2006) and biosand filters (see Duke et al. 2006; Stauber et al. 2006), the contribution of any one particular determinant may be low, resulting in the low coefficients of determination reported below. However, the findings at the significance level of $\alpha = 0.01$ with $n = 24$ suggest the variables and measures of outcome are linearly related.

As shown in Fig. 4, the LR of *E. coli* across the biosand filter is related to the log of source water contamination (0.56, $R^2 = 0.42$, $p < 0.01$), as is the log of filtered water contamination (0.44, $R^2 = 0.31$, $p < 0.01$). This result indicates that the biosand filter follows the model, described by Hendricks and Bellamy (1991), of the linear relationship between the magnitudes of influent and effluent concentrations of heterotrophic bacteria in a traditional slow-sand filter. More importantly, it also clearly demonstrates that while filter performance is increased at greater source contamination, the filtered water contamination is nonetheless increased. Therefore, consideration of the source water quality is important when evaluating whether to use the biosand filter technology for achieving clean water.

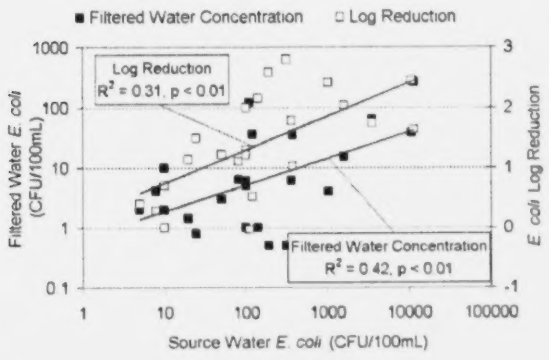

Fig. 4. Correlation between source concentration, filtered concentration, and log reduction for E. coli.

The relationship between hydraulic loading rate and filtration efficiency in a traditional slow-sand filter is described in detail by Hendricks and Bellamy (1991) and Pyper and Logsdon (1991). These sources indicate that filtration efficiency improves at lower hydraulic loading rates. This relationship between flow rate and filter performance was detected for the biosand filters evaluated in this field study, as shown in Fig. 5. The peak hydraulic loading rate was found to have a negative effect on the LR of total coliforms (–1.46, $R^2 = 0.45$, $p < 0.01$), *E. coli* (–0.93, $R^2 = 0.31$, $p < 0.01$), and turbidity (–0.68, $R^2 = 0.28$, $p < 0.01$). This correlation was most significant for total coliforms, where the mean LR was 2.2 (SD = 0.93) for those filters with peak hydraulic loading rates below 0.6 $m^3/m^2/h$, and only 1.3 (SD = 1.0) for those with greater peak hydraulic loading rates; this difference is significant at the $\alpha = 0.05$ level. Even though the biosand filter operates under a falling head condition, the results indicate that the hydraulic loading rate is still an important determinant of filter performance, akin to the slow-sand filter. A simplified model for explaining this phenomenon involves the relationship between pore-size in the biological layer; the screening, adsorption, and biological processes for pathogen inactivation within the layer; and the permeability of the layer as described by Darcy's Law.

Laboratory studies have demonstrated that the flow rate through a biosand filter decreases over time as the biological layer develops (Buzunis 1995; Stauber et al. 2006). The time period since the last washing of the biological layer is therefore considered a determinant of the flow rate. Household members can ensure that their filters operate at the recommended flow rate by carefully regulating the frequency of filter maintenance. Unfortunately, much confusion was observed among the filter users in Posoltega regarding filter maintenance, suggesting insufficient user training. The users were divided almost equally into three groups: those that wash their filter when the flow is slow; those that wash their filter when the top appears dirty; and those that wash their filter on a regular schedule. The reported maintenance frequency, which varies from every second day to once every six months, averaged at 39 days (SD = 36). This suggests that filter users would benefit from training that included a more clearly defined maintenance frequency. While the optimum maintenance frequency for a particular filter is dependent upon many factors, including source contamination and daily use, the data suggest that allowing upwards of six months between maintenance cycles will not be detrimental to filter performance.

As shown in Fig. 6., the standing depth of water (in cm) over the top of the sand during the pause period when there is no flow was found to have a positive effect on the LR of total coliforms (0.10, $R^2 = 0.35$, $p < 0.01$) and *E. coli* (0.10, $R^2 = 0.49$, $p < 0.01$). Buzunis (1995) recommended that the standing depth of water be minimized so as to maximize the diffusion of oxygen through the water depth to the biological layer during the

static period. The contrary results of this study suggest that other mechanisms may play a more significant role in filter performance than the oxygen transfer across the standing depth of water. Further investigation with a larger sample size of operational filters in the field is recommended.

No statistically significant relationship was detected between the total daily filtered volume and the filter performance (LR of total coliforms, *E. coli*, and turbidity, $p > 0.05$, data not shown). Biosand filters shared between different households were used to filter greater quantities of water, up to six buckets (120 L) per day. Yet, these filters were found to perform at the same level as those used to filter one bucket per day. This result suggests that sharing available filters in communities where access is limited may be a feasible option. Such a practice would encourage safe water behaviour among those individuals that are not currently filter users, thus contributing positively to community development.

No differences in performance were detected between filters constructed from different materials (plastic or concrete), installed in different years, or placed in different communities (LR of total coliforms, *E. coli*, turbidity, $p > 0.05$, data not shown). The finding that filter performance was unaffected by its structural composition is not surprising. The structural component is merely a container for the filter media, and only needs to be structurally sound in order for the filter to function. The finding that filters implemented in different years (i.e., 1999 or 2004) performed equally well suggests that long-term filter performance can be expected to remain constant, provided that the filter is used consistently and the structure remains sound.

In future studies, testing a random sample from a larger population of filters constructed from different materials, exposed to different usage habits and operational parameters, and placed in different communities would enable multiple comparisons and interactions of tested variables, and may yield additional information.

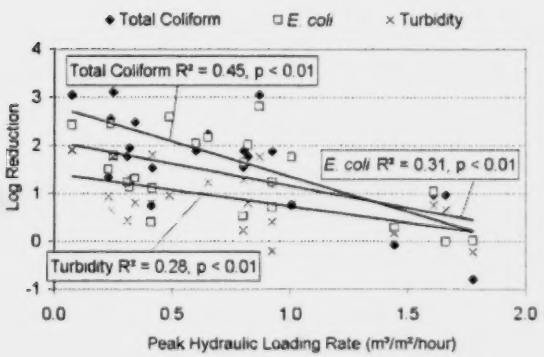
◆ Total Coliform
□ E. coli
× Turbidity
Total Coliform R² = 0.45, p < 0.01
E. coli R² = 0.31, p < 0.01
Turbidity R² = 0.28, p < 0.01
Log Reduction
Peak Hydraulic Loading Rate (m³/m²/hour)

Fig. 5. Log reduction versus peak hydraulic loading rate.

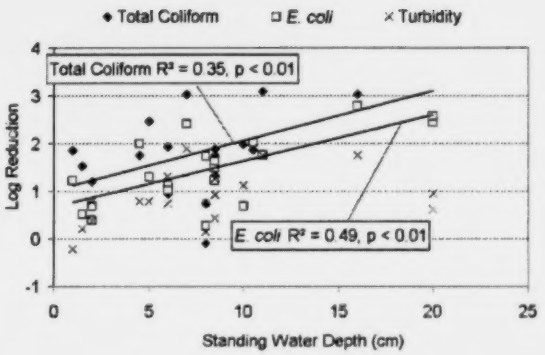

Fig. 6. Log reduction versus standing water depth.

Sustained Use of the Biosand Filter

The results of the questionnaire indicated insufficient user training and a lack of follow-up on the part of the implementing NGO. With a proper feedback mechanism, many of the problems (discussed below) could have been identified and rectified. The implementation of biosand filters in Posoltega, Nicaragua, represents a failed attempt at introducing a positive change in community development, as indicated by the low rate of sustained filter use (10%). The distribution of the 234 filters installed in Posoltega and the 24 found to still be in use is displayed in Table 2. The separate rates of sustained use for the 1999 filters and 2004 filters are 30 and 7%, respectively. The remaining filters were found to be in various states of disuse and disrepair: cracked, leaking, broken, dismantled, emptied, or otherwise abandoned and unused.

Failure mechanisms of 1999 filters. Of the 34 filters installed in the community of El Trianón in 1999, only 10 were found to still be in operation. Of the others, 14 were broken, 7 were abandoned, and 3 were in functional condition, but were not actually in use (e.g., locked away inside the storage room of the local school). Filters failed

TABLE 2. Summary of sustained use of the biosand filter in Posoltega, Nicaragua

	Biosand filters installed		*Biosand filters in use as of 2007*	
Installation year:	*1999*	*2004* [a]	*1999*	*2004*
El Trianón	34	20	10	5
San Gilberto	–	50	–	1
Posolteguilla	–	50	–	2
Buenos Aires	–	10	–	3
El Mojón	–	50	–	3
San Agustín	–	20	–	0
Total:	34	200	10	14

[a] Distribution of 200 filers from 2004 estimated according to R. Hernández, MINSA Posoltega (personal communication, January 22, 2007).

as a result of cracks developing in the structural body of the concrete filters, and outlet pipes becoming dislodged from the plastic filters.

Many of the 1999 filters reportedly broke when families tried to move them to a new community location following Hurricane Mitch. While the relocation was still underway, some families received filters at their homes in the original community location. When these families moved to their new homes, many of the filters were damaged during the transition. Other filters were abandoned altogether at the old homes when the families moved to their new homes or away from El Trianón completely.

The implementation of new biosand filters in 2004 and their subsequent failure was another indirect cause of failure of some of the filters from 1999. In these cases, the families in El Trianón that received a second filter in 2004 disassembled or abandoned their otherwise operational 1999 filter; when the 2004 filter failed, the family was left without any operational filter to use.

Failure mechanisms of 2004 filters. The most common reason for failure in the biosand filters from 2004 was significant cracking in the concrete walls, which resulted in water and sand leaking out of the filters. Even minor cracks caused water to drain below the top layer of sand, thus preventing the proper development of the biological layer. Leaks would also cause water to run on the ground or floor, creating an inconvenience to the user. With few exceptions, the leak in the structure prompted users to stop using the filter altogether, and to resume drinking water directly from the well.

The actual cause of the high incidence of cracking of the 2004 filters is not known with certainty at this time. Anecdotal evidence suggests that the concrete was not given sufficient curing time to achieve any significant strength and durability. Every individual interviewed regarding the filter construction activities indicated that filters were removed from their molds after one day of curing and almost immediately loaded onto carts to be transported across rural dirt roads to the communities. Many people from the community of San Gilberto made reference to "*el golpe*" ("the impact") which further suggests a callous unloading procedure upon arrival at the destination household.

The difference in long-term durability between the 1999 and 2004 filters is likely a reflection of the fact that the 2004 filters were built by community members under the direction of the NGO technicians at the health center where quality control would be more difficult to maintain than in a dedicated facility in Managua. This indicates the importance of strict quality control during filter construction to ensure long-term successful use of the biosand filter.

Conclusions

This paper presents an evaluation of the biosand filters that were installed in Posoltega, Nicaragua in 1999 and 2004. The study was an evaluation of the in situ technology to characterize the condition of existing filters, determine the filter performance of operational filters, and identify the determinants of long-term use and performance of the technology. The major findings of the study are as follows:

- Of 234 filters installed, 24 were found to be in use. The rate of sustained use was 10%.
- Mean LRs of 1.73 for total coliforms, 1.36 for *E. coli*, and 0.91 for turbidity were determined. The equivalent percent removal was 98% for total coliforms, 96% for *E. Coli*, and 88% for turbidity. This is consistent with slow-sand technology, and other laboratory and field studies of the biosand filter.
- Source water quality is an important determinant of filtered water quality and filter performance. The biosand filter cannot deliver clean water as defined by WHO standards in isolation of consideration of source water quality and/or additional treatment involving disinfection.
- The peak hydraulic loading rate and the standing depth of water were also identified as important determinants of filter performance.
- No differences in filter performance were detected in filters from 1999 compared with filters from 2004. This suggests no long-term decrease in filter performance.
- For the other 90% of filters not in use, the greatest cause of failure was cracking of the concrete structure, likely a result of poor quality control during implementation.

The major findings from this evaluation indicate that implementation of household water treatment technology can fail if basic quality control is not practiced. However, in spite of the inadequate training of the users, this evaluation demonstrated the biosand filter technology to be robust. The 24 biosand filters were performing as expected in removing nearly 2 log units of coliform bacteria, eight and three years after implementation.

Acknowledgments

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Evaluation of Field Testing Techniques Used in a Household Water Treatment Study in Posoltega, Nicaragua

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A field evaluation of biosand filters, a method of household water treatment, was conducted in Posoltega, Nicaragua. The evaluation consisted of water quality testing for *Escherichia coli* and total coliforms using membrane filtration (MF) with m-coliBlue24 growth media, and SolarCult dipslides. For each sample tested, the MF procedure was applied to two volumes differing by an order of magnitude to capture the expected range of microbial contamination. A follow-up laboratory quality assurance/quality control procedure was undertaken to validate the field methods. The average coefficient of variation was 51%, with no statistically significant difference between the field and laboratory data. The MF procedure used with m-coliBlue24 produced useful reproducible results for the microbial concentrations encountered in the field. Dipslide results were found to correlate poorly to the membrane filtration results from the field, and should not be used to test drinking water due to the high limit of detection. They may still be useful for preliminary testing of highly contaminated source water as part of a household water treatment project. Dipslides may also be a useful tool for local health representatives to promote safe water practices within the community since they are simple to use and provide a visual indicator of water quality.

Key words: **biosand filter, household water treatment, field water quality testing, m-coliBlue24, SolarCult Dipslides, developing countries, Nicaragua.**

Introduction

The World Health Organization (WHO) reports that there are 1.1 billion people worldwide without access to safe drinking water and there are 1.6 million deaths every year attributable to lack of access to safe drinking water and basic sanitation (WHO 2005). The majority of these deaths occur in rural and remote areas of developing countries, where communities are often at higher risk due to contaminated water supplies and a lack of water treatment. Household water treatment (HWT) has been advocated as a solution to this global problem, wherein a family takes responsibility for the treatment of their own drinking water through the application of a household-based technology.

The evaluation of HWT technology typically relies on measuring the quantitative reduction of contaminants and/or indicator organisms achieved by the technology. Undertaking microbial water quality testing in rural and remote areas of developing countries as part of the evaluation requires consideration of the setting in which the testing will be conducted. This setting can include a lack of access to laboratory facilities, financial and resource constraints, and a finite quantity of consumable materials that can be transported to the site, thereby limiting the number of tests that can be performed. Nonetheless, the ability to produce reliable and accurate water quality data in these settings is important for the evaluation of HWT in assessing the ability of a particular technology to address the global problem of access to safe water. A case study illustrating this scenario is presented here.

The biosand filter is a form of HWT technology based on slow-sand filtration at a scale that is appropriate for a single household (Manz et al. 1993; Buzunis 1995). Laboratory evaluations of the biosand filter have demonstrated its ability to consistently remove up to 2 log units of faecal coliforms (Buzunis 1995) and *Escherichia coli* (Stauber et al. 2006), and up to 4 log units of *Giardia* cysts and *Cryptosporidium* oocysts (Palmateer et al. 1999). Various field evaluations have also demonstrated the ability of the biosand filter to consistently remove pathogens from drinking water at the household level in rural communities in the Dominican Republic (Stauber et al. 2006), Haiti (Duke et al. 2006), and Ethiopa (Earwaker 2006).

Thirty-four biosand filters were introduced into the remote community of El Trianón, in the Municipality of Posoltega, Nicaragua, in 1999 as an emergency aid to provide clean drinking water to families impacted by Hurricane Mitch (Baughen et al. 1999). In 2004 the program was expanded to install 200 more filters across six rural communities in Posoltega. A schematic of the types of biosand filters installed in Posoltega, Nicaragua is shown in Fig. 1. Families in this agricultural area typically rely on individual hand-dug shallow wells for their source water; previous studies have shown these wells to be contaminated with enteric pathogens and pesticides (CIRA 1999a, 1999b). A map of the study area is shown in Fig. 2.

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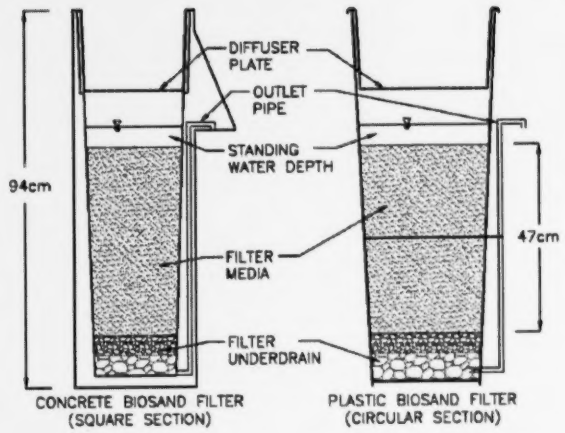

Fig. 1. Schematic of the biosand filters installed in Posoltega, Nicaragua.

A field study was conducted from January to April 2007 to evaluate the biosand filters installed in Posoltega, Nicaragua. The findings of the evaluation are presented in Vanderzwaag et al. (2009). An evaluation of the field water quality testing used to determine microbial removal efficiency as part of the evaluation is presented in this paper.

The constraints faced in the biosand filter evaluation in Posoltega, Nicaragua included the remote locations of the communities where the biosand filters were installed and the lack of a convenient laboratory facility for processing water samples. The opportunities included in-kind contributions of a field water testing kit for performing field membrane filtration (MF) by the Center for Affordable Water and Sanitation Technology (CAWST), and access to a small work space including refrigeration, electrical power, and daily access to hot-air sterilization by the Alma Nubia Lopez Health Center of Posoltega. The health center also provided the use of a motorized,

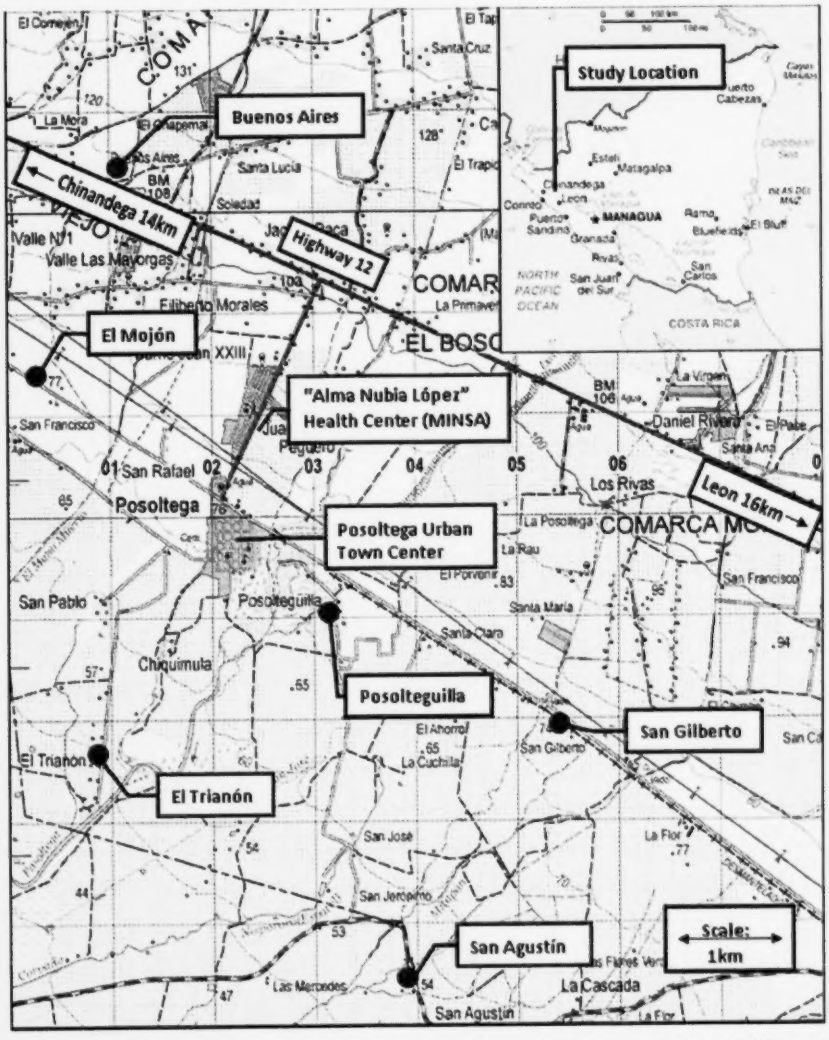

Fig. 2. Map of Posoltega and study communities. Sources: United States Department of State (2007) & INETER (2006).

three-wheeled rickshaw for transportation to the remote communities where the filters were installed. Protocols were developed within the context of these constraints and opportunities to carry out field water quality testing, including the sterilization of field equipment, accurate measurement of sample volumes, production of sterile rinse water, incubation of the prepared membranes, and enumeration of the results.

It was acknowledged that most laboratory water quality testing protocols are for the isolation and identification of indicator organisms in high quality finished water. Preliminary testing and available background data (CIRA 1999a, 1999b) indicated that the source water in Posoltega was highly contaminated. The protocol used in the evaluation therefore involved the filtration of volumes of different orders of magnitude in order to accommodate and produce useful and enumerable results across several orders of magnitude of microbial concentration in the source and finished water.

Materials and Methods

The methods are separated between the field methods used during the evaluation of the biosand filters in Posoltega, Nicaragua, and the laboratory methods used in a follow-up protocol in a controlled setting at the University of British Columbia.

Field Methods

The field methods included identifying households where a biosand filter had been installed and was still in operation, acquiring consent from these households for their participation in the study, administering a questionnaire regarding water and sanitation practices around the home, and testing water quality.

At each household, samples for water quality testing were taken from the source water before it was introduced into the top of the biosand filter, from the filtered water immediately leaving the spout of the biosand filter, and from the storage container of filtered water currently being used as the family's source of drinking water. Each sample was tested for *E. coli* and total coliforms using membrane filtration. In addition, the source water and stored water were tested for microbial contamination using dipslides.

Membrane filtration (MF). MF was used to test the water for coliform bacteria. The MF technique used was based on Standard Method 9222: Membrane Filter Technique for Members of the Coliform Group (APHA et al. 2005). The equipment used was the Potatest WE10005 (Wagtech International, Berkshire, U.K.). This equipment allowed for the procedure to take place in the field rather than transporting the water samples to a central laboratory facility. Field sterilization of the equipment was achieved with isopropyl alcohol wipes and through the combustion of methanol (Fisher Chemicals #A4524, Fisher Scientific, Pittsburg, Pa.) as per the Potatest operation manual (Wagtech International [no date]). A hand operated vacuum pump was used to draw water through a mixed cellulose ester membrane filter of pore size 0.45 µm (Fisherbrand #09-719-555, Fisher Scientific, Pittsburgh, Pa.). The membranes were then placed in sterilized aluminum Petri dishes (Wagtech #WAG-WE10406, Wagtech International, Berkshire, U.K.) on an absorbent pad (Millipore #AP10045S0, Millipore Corp, Billerica, Mass.) that had been saturated with 2 mL of growth media.

The growth media selected for this study was m-coliBlue24 (Hach, Loveland, Colo.). The differential media contains enzymes which cause coliforms to produce red colonies by their ability to reduce TTC (2,3,5-triphenyltetrazolium chloride), and *E. coli* to produce blue colonies by their ability to hydrolyze the enzyme substrate BCIG (5-bromo-4-chloro-3-indolyl-beta-D-glucuronide) to an insoluble salt while suppressing the growth of noncoliform organisms (Hach Company 1999). Prepackaged in 2-mL ampoules, there was no requirement for media preparation and portioning, and no risk of contaminating the media. A limitation of the m-coliBlue24 is that it must be stored between 2 and 8°C, and thus access to refrigeration at the local health center was an important consideration in the choice of this medium.

A variation from the Standard Method was the filtration of different volumes of test water where the anticipated number of organisms in 100 mL would be too high to produce evaluable results. Sample volumes of 1 and 10 mL were taken of the source water, and sample volumes of 10 and 100 mL were taken of the filtered and stored water. The 1-mL samples were measured using sterile, single-use plastic pipettes (Fisherbrand #13-711-20, Fisher Scientific, Pittsburgh, Pa.), the 10-mL samples were measured using sterilized 10-mL Kimax beakers (Kimble #14000-10, Kimble Glass, Vineland, N.J.), and the 100-mL samples were measured by filling the reservoir tube (funnel) on the membrane filtration equipment to an indicated mark. The measuring equipment was then flushed with sterile water. Of each water sample, the smaller volume was always filtered first to avoid unnecessarily repeating the flame sterilization; the number of any remaining organisms from the smaller volume would not significantly affect the concentration of organisms of the larger volume.

The colonies on the membranes were incubated for 24 hours at 35 ± 0.5°C. The AC-powered incubator included with the Potatest WE10005 equipment was kept at the health center where it was plugged into a standard 110V AC wall outlet (a transformer was used to convert to the 220 V AC required for the equipment, and an accompanying rechargeable battery pack maintained power during the frequent power outages). The time period between placing the membrane into the Petri dish and placing the Petri dishes into the incubator was

between 1 and 4 hours, allowing sufficient time for a recovery period for the microorganisms on the membrane. After the incubation period, the colonies that formed on the membrane were enumerated with the assistance of a 5× magnification handheld lens and a tally counter. A digital photograph was also taken of each series as part of record keeping.

Two "blank" samples were prepared every day to confirm the sterilization procedures, representing 11% of all of the samples taken. The sterile water used for rinsing and the preparation of "blank" samples was prepared nightly by boiling commercial bottled water (Fuente Pura, Managua, Nicaragua), covering it, and then allowing to cool overnight. The rinse bottles themselves were sanitized using a 70% rubbing alcohol solution purchased from a local pharmacy and allowed to air dry inverted overnight.

The 10-mL beakers and the aluminum Petri dishes were wrapped in aluminum foil and sterilized in a dry-air oven for 30 minutes at 300°C prior to use each sampling day. All of the waste materials from the MF procedures were incinerated at the Posoltega health center.

SolarCult dipslides. SolarCult dipslides (Solar Biologicals, Ottawa, Ont.) were used to test the source water and store postfiltered water. The dipslides consisted of a plastic paddle coated with growth media, attached to a handle/cap that fit a self-containing clear plastic vial. One side of the paddle was coated with nutrient agar to which TTC was added for the detection of heterotrophic bacteria, and the other side was treated with MacConkey agar for the detection of Gram-negative organisms (Solar Biologicals 2006).

The paddle was dipped into the water sample for three seconds and returned to the vial, and the cap was closed sufficiently to prevent contamination but allow air exchange. The vials were incubated at room temperature which ranged between 25 and 30°C. After approximately 48 hours, the colonies formed on either side of the dipslide were enumerated. The dipslides were disposed of by filling each vial with household bleach, sealing the cap, and incinerating them at the Posoltega health center.

It was acknowledged that the SolarCult dipslides are intended as a visual reference for industrial use, and are not recommended for drinking water testing due to their high limit of detection. However, their simplicity in use and visual interpretation suggested that they may have a role in water quality testing that was worth investigating in remote locations where other resources are not available.

Laboratory Methods

In order to provide a level of confidence in the results produced in the field, a quality assurance / quality control (QA/QC) procedure was undertaken in a controlled laboratory setting at the School of Environmental Health at the University of British Columbia. The specific objectives of the QA/QC work were to identify and estimate the sources of error associated with the methodology used in the field. The methods consisted of preparing spiked solutions inoculated with known concentrations of indicator organisms, and applying the same water quality testing techniques used in the field with regard to both the membrane filtration and the dipslide protocols. The correlation of the MF results to the expected organism concentration was then determined. The errors associated with volume measurements and with enumerating colonies from samples tested at the same volume and across different volumes were also quantified. In addition, colonies growing on the m-coliBlue24 media were isolated and identified for confirmation of the differential count.

Preparation of test solutions. The QA/QC work was based on prepared solutions inoculated with a known concentration of indicator organisms. From the preliminary results from the field water quality testing, the prepared test solutions needed to cover a range from approximately 10 to 1,000 CFU/100 mL for *E. coli*, and 1,000 to 100,000 CFU/100mL of total coliforms. For the purpose of the laboratory work, *E. coli* (ATCC #25922) and *Salmonella enterica* (ATCC #29058) were chosen as representative of faecal contaminants of water. A third organism, *Enterococcus faecalis* (ATCC #29212) was included in the prepared solutions to mimic a background organism suppressed by the m-coliBlue24 as well as on the dipslide MacConkey agar, but would be detected by the TTC on the reverse of the dipslide. The *E. faecalis* was inoculated into the solution at a concentration several orders of magnitude greater than that of the other two organisms, such that if the suppression of its growth failed, the noncoliform background would be readily detected.

The test solutions were prepared by making a neat suspension from colonies of the desired organism from an agar plate. The suspension was adjusted until the optical density (OD_{360}) measured with Ultrospec II (LKB Biochrom, Cambridge, U.K.) was between 0.5 and 1.5, corresponding to a range of 10^8 to 10^9 bacteria per millilitre. Serial ten-fold dilutions were performed from the neat suspension as described in Standard Method 9215: Heterotrophic Plate Count (APHA et al. 2005), and three aliquots of 0.1 mL of the fifth dilution were dispersed and spread onto plates of Tryptic Soy Agar (TSA) (Difco, Becton, Dickenson and Company, Sparks, Md.). The average count from these three plates was used to predict the concentration of the neat sample suspension, and hence the final concentration of the spiked test solution. For the purpose of this study the outcome of this method was considered to be the "true" concentration of the test solution.

Nine test solutions were prepared and tested by MF a total of nine times: three times each for the sample volumes of 1, 10, and 100 mL. Each solution was also tested with

three dipslides. The water quality testing techniques used were identical to the field methods, including the use of the Potatest equipment for the MF procedure (including sterilization and volumetric measurement) and incubating the prepared membranes, the preparation of the sterile rinse water, and the application of the dipslides.

Volumetric measurement. The specific volumes of 1, 10, and 100 mL as measured in the field were confirmed by gravimetric analysis using top-loading balances (Sartorius, Mississauga, Ont.). Five randomly selected 1-mL pipettes and all eleven 10-mL Kimax beakers used in the study were tested five times each by filling to the indicated mark and recording the mass of the collected water sample. The 100-mL reservoir tube on the membrane filtration equipment was similarly tested a total of eight times, with a new membrane filter in place for each test.

Colony identification. An external water source (duck pond at Jericho Beach in Vancouver, B.C.) was tested using the MF technique with the m-coliBlue24 growth media. Six blue colonies (suspect *E. coli*) were subcultured onto Eosin methylene blue (BBL, Becton, Dickinson and Company, Sparks, Md.) agar, and five red colonies (suspect coliform) were subcultured onto TSA, repeating as required until pure cultures were obtained. Suspensions were then prepared of each culture, and API 20E test strips (bioMérieux, St. Laurent, Que.) and the corresponding online application APIWEB (bioMérieux, St. Laurent, Que.) were used to identify the cultures as per the included directions.

Statistical Methods

The coefficient of variation was used to quantify the error associated with the individual procedures, and Student's *t*-tests (two-tailed heteroscedastic) were used to determine the statistical significance of the difference between data sets, or the statistical significance of a correlation between variables. The coefficient of variation is the normalization of the standard deviation by the mean and is therefore an appropriate measure of the error because both the organism concentration and the actual filtered volume varied across multiple orders of magnitude between tests.

Results

Laboratory Results

Correlation to spiked concentration. The results of the MF procedure were compared with the predicted spiked organism concentration for *E. coli* and *Salmonella*, and the ratio between the concentrations was calculated (Table 1). This ratio was found to vary between 0.16:1 and unity, with an average of 0.41:1 (standard deviation [SD] = 0.28:1). There were no statistically significant differences between the *E. coli* and *Salmonella* results. The linear regression between the concentration predicted by the MF technique and the actual concentration was statistically significant at the $\alpha = 0.01$ level.

Volumetric variation. The mean, coefficient of variation, and statistical significance of the systematic bias of the methods used to measure the sample volumes are displayed in Table 2.

TABLE 1. Comparison of MF results with spiked concentrations [a]

	Sample Number:	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*
E. coli										
	Spiked concentration:	12	–	79	–	950	160	97	580	480
MF Results [b]	1-mL mean result	ND	–	ND	–	500	200	ND	100	ND
	10-mL mean result	10	–	80	–	280	30	10	30	90
	100-mL mean result	5	–	80	–	333	57	16	224	118
MF Concentration [c]		5	–	80	–	280	57	16	224	118
Ratio of MF to spiked concentration		*0.42:1*	–	*1.0:1*	–	*0.30:1*	*0.36:1*	*0.16:1*	*0.39:1*	*0.25:1*
Salmonella										
	Spiked concentration:	–	1,700	–	16,000	–	1,400	18,000	1,400	13,000
MF Results [b]	1-mL mean result	–	500	–	15,900	–	700	3,000	200	4,400
	10-mL mean result	–	730	–	12,600	–	410	3,560	80	6,020
	100-mL mean result	–	676	–	TNTC	–	652	TNTC	289	TNTC
MF Concentration [c]		–	730	–	15,900	–	410	3,000	289	4,400
Ratio of MF to Spiked concentration		–	*0.42:1*	–	*1.0:1*	–	*0.30:1*	*0.17:1*	*0.21:1*	*0.34:1*

[a] ND = not detected; TNTC = too numerous to count.
[b] The average of the three plate counts from each sample volume is reported in CFU/100 mL.
[c] The MF Concentration was computed from the single plate count between 15 and 150 CFU where possible, or the otherwise nearest and most appropriate, as suggested in Fig. 7.

TABLE 2. Gravimetric analysis of volume measurements

Nominal volume (mL)	*Mean measured mass (g)*	*Coeff. of var.*	*Systemic bias*	*Statistical significance*
1	0.982	4.3%	-1.8%	$p < 0.05$
10	10.74	2.6%	+7.4%	$p < 0.01$
100	104.0	0.8%	+4.0%	$p < 0.01$

Coefficient of variation. The coefficients of variation between the three individual plate counts from each filtered volume of each sample were computed. No statistically significant difference was detected between results for the type of organism (*Salmonella* versus *E. coli*), nor for the sample volume. Because of the lack of effect, the data set was aggregated based on the unfactored plate count mean. The average coefficient of variation from the plate count was determined to be 38% (SD = 23%). Furthermore, a statistically significant negative correlation was detected between the coefficient of variation and the logarithm of the mean plate count at the $\alpha = 0.05$ level (Fig. 3).

For each test solution and filtered volume, the triplicate plate counts were averaged and factored according to the filtered volume. A new coefficient of variation was then computed between the counts from the 1- and 10-mL samples, and again between the 10- and 100-mL samples. This was to mimic the field methodology, where each water sample was tested at either 1- and 10-mL volumes, or 10- and 100-mL volumes. Each computed coefficient of variation was treated as a separate observation.

No statistically significant difference was detected between the computed coefficient of variation between filtered volumes for the type of colony (*Salmonella* versus *E. coli*), nor between the results computed between the 1- and 10-mL volumes versus the 10- and 100-mL volumes. Because of the lack of effect, the data set was again aggregated. The average coefficient of variation computed across the different filtered volumes was 44% (SD = 31%).

Colony identification. Of the six blue colonies suspected to be *E. coli*, five were successfully identified as such using the API 20E test strips and the corresponding APIWEB online application. The sixth colony was identified as *Klebsiella pneumoniae spp pneumoniae* with 97.5% certainty. The incidence of false positives is reportedly 3% for *E. coli* (Grant 1997).

Of the five red colonies suspected to be coliforms, three were identified as *Klebsiella oxytoca*, one as *Enterobacter cloacae* and one as *Raoultella ornithinolytica* (formerly classified as *Klebsiella ornithinolytica*). These are all Gram-negative, rod shaped bacteria (Bergey and Holt 1994), which were correctly identified as members of the coliform group by the m-coliBlue24 growth media.

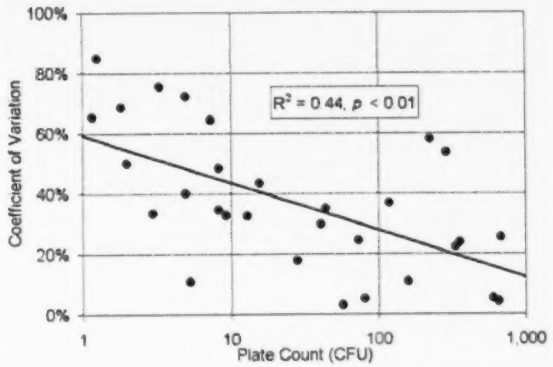

Fig. 3. Coefficient of variation versus plate count.

SolarCult dipslides. The results from the SolarCult dipslides were compared with the spiked concentrations in the test solutions (Fig. 4). The colony counts from the MacConkey side of the dipslide were plotted against the total spiked concentration of Gram-negative organisms in the test solutions (*E. coli* and *Salmonella*), and the colony counts from the TTC side of the dip slide were plotted against the total spiked concentration of microorganisms in solution (i.e., *E. faecalis*). The regression line through both data sets is statistically significant at the $\alpha = 0.01$ level, although this is dominated by the correlation between the higher TTC counts and the *E. faecalis*. The lower limit of detection of the dipslides predicted by the regression line is approximately 1,000 CFU/100 mL.

Field Results

A total of 255 field samples were tested for both *E. coli* and total coliforms by MF with m-coliBlue24 growth media; 92 of these were of source water, 85 of filtered water, and 78 of stored water. The results of the field testing (Fig. 5) indicate that the biosand filters were achieving nearly 2 $\log_{10}$ reduction units. Unfortunately, the stored postfiltered water was approximately a full order of magnitude greater than the filtered water, suggesting problems with regrowth and recontamination. In general, neither the filtered water nor the stored water met the WHO guidelines for safe drinking water (WHO 2006). A further discussion of the biosand filter evaluation can be found in Vanderzwaag et al. (2009).

Coefficient of variation. The field methodology included testing duplicates of water samples at different volumes to cover a broad range of possible concentrations and to provide a level of confirmation of the results. Of these, there were 179 pairs of tests (358 results) where both the larger and smaller sample volumes yielded enumerable results: 104 pairs for *E. coli* and 75 pairs for total coliforms. The average coefficient of variation computed between the results from the corresponding pairs of larger and smaller volumes was 51% (SD = 35%). No

statistically significant difference was detected between this coefficient of variation from the field data and the corresponding computation from the laboratory data.

SolarCult dipslides. Figure 6 displays the colony counts from the MacConkey agar side of the dipslide plotted against the total coliform concentration (including *E. coli*) determined by MF for the corresponding water sample. The regression line through the data set is not statistically significant. This is the result of the fact that the MacConkey agar is more permissive, and will identify Gram-negative but noncoliform bacteria in the water sample that are not detected by the m-coliBlue24 growth media. The controlled tests in the laboratory did not include any of these other organisms, and hence the laboratory data forms an approximate upper bound for 91% of the field data, as shown in the figure.

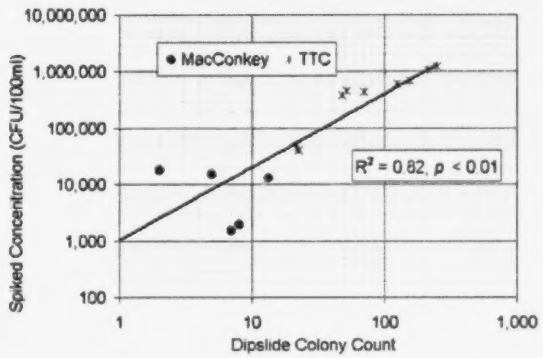

Fig. 4. Correlation of dipslide colony count to spiked concentration.

Discussion

The water quality testing methods employed for this study were successful in yielding useful, reproducible numeric results within the context of the constraints and opportunities encountered in the field during the evaluation of biosand filters in Posoltega, Nicaragua.

Membrane Filtration Using m-coliBlue24

The MF procedure using m-coliBlue24 allowed for the enumeration of *E. coli* and total coliforms up to concentrations of 100,000 CFU/100 mL in source water while maintaining a detection threshold of 1 CFU/100 mL in filtered water. The results of the QA/QC suggest that the MF technique tended to underestimate the actual concentration. This may be due to a variety of factors, including organisms that are stressed or even killed on the membrane during the membrane filtration, or organisms clinging to the interior equipment walls in spite of the rinsing techniques. Nonetheless, the MF technique appeared to be accurate to an order of magnitude level of precision, which was sufficient for the purposes of this study.

From the arbitrary sample of duck pond water, five of the six blue colonies were successfully identified as *E. coli,* and all of the red colonies were identified as species belonging to the coliform group using the independent method of the API 20E test strips. Coupled with the successful suppression of *E. faecalis* as a background organism, this outcome leads to a very high level of confidence that the organisms identified through the MF technique using the m-coliBlue24 are in fact the indicated type of organisms. The reported rate of false positives for m-coliBlue24 is 3% for *E. coli* and 27% for coliforms (Grant 1997).

Specific to the field methodology and equipment used in this study, a bias of up to 7% was detected from the volumetric measurement techniques. While statistically significant, this bias is relatively small in comparison

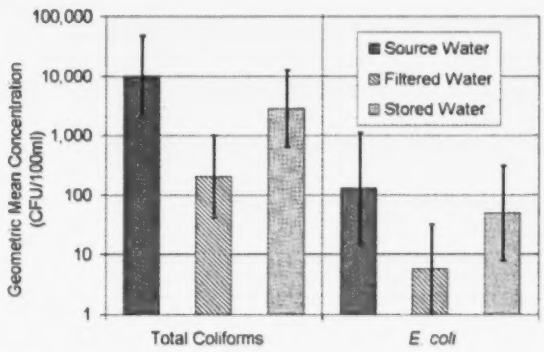

Fig. 5. Biosand filter evaluation microbial results. Error bars indicate one geometric standard deviation.

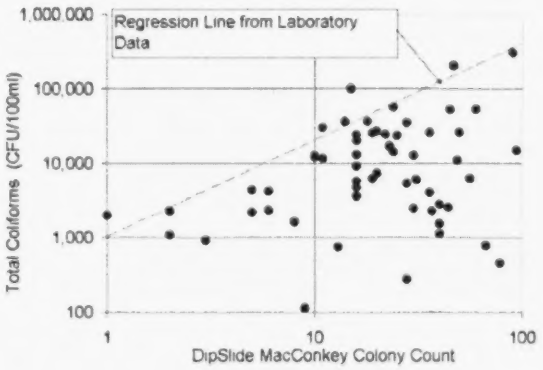

Fig. 6. Correlation of MacConkey agar colony counts to field MF results.

with the random error associated with individual plate counts or averaging the results derived from testing across different sample volumes; therefore, no correction was applied. The average coefficient of variation associated with any plate count was 38%. The average coefficient of variation associated with averaging across different sample volumes was found to be 44% in the laboratory and 51% in the field. No statistically significant difference was detected between the laboratory and field data set, suggesting that the study results would not have had any less random error had the water samples been collected and transported to a controlled laboratory facility for testing.

The random error associated with the MF technique can be reduced by recognizing the relationship between the maximum coefficient of variation and the plate count. This can be observed by plotting a bounding curve on the plate count data presented in Fig. 3. This curve is minimized at approximately 50 CFU, with a maximum expected coefficient of variation of 35%. That there was no statistically significant effect from the filtered volume on this data set suggests that this bounding curve exists for each sample volume, as plotted in Fig. 7. The choice of how to compute the concentration of the test sample is then dependent on the plate count from each volume, where a plate count between 15 and 150 CFU is desired. This concept is very similar to Standard Method 9222: Membrane Filter Technique for members of the Coliform Group (APHA et al. 2005), which recommends targeting a plate count between 20 and 200 CFU. Some forehand knowledge of the approximate order of magnitude of microbial levels is required to know what sample volume to use for the MF; this is further compounded when both indicator organisms of *E. coli* and total coliforms are desired. The methodology used in this study, testing 1 and 10 mL for source water and 10 and 100 mL for filtered and stored water, was found to produce useful results for the conditions encountered in the field.

A limitation of MF with m-coliBlue24 is the occurrence of growth on the membrane which can be difficult to interpret. Examples of this include smudging and/or dry patches on the membrane, growth around the perimeter of the membrane, colonies of nonuniform sizes (in particular a "dusting" of tiny colonies across the membrane along with the standard-sized colonies growing on the membrane), colourless confluent growth across the membrane, and *E. coli* forming black rather than blue colonies. These types of results occurred in approximately 5% of the tests conducted. The smudging and perimeter growth can be controlled through careful techniques used in the field. The dusting of tiny colonies and the colourless confluent growth were replicated in the laboratory under circumstances where the number of *Salmonella* organisms was in excess of 10,000 CFU and the background organism of *E. faecalis* was in excess of 400,000 CFU in the 100-mL test sample. For this reason it is important to have a trained individual interpret the MF results to avoid the danger of misinterpreting colourless growth as an organism concentration of zero rather than as truly being too numerous to count. It is suspected that temperature effects during the storage and transportation of the m-coliBlue24 may be related to the black *E. coli* colonies being formed instead of blue. A further investigation into the temperature effects on the growth media is required to further demonstrate the applicability of using m-coliBlue24 for field water testing in developing countries where maintaining the temperature between 2 and 8°C during storage and transportation may be difficult.

SolarCult Dipslides

As shown in Fig. 6, the SolarCult dipslides results exhibited poor correlation to the MF results in the

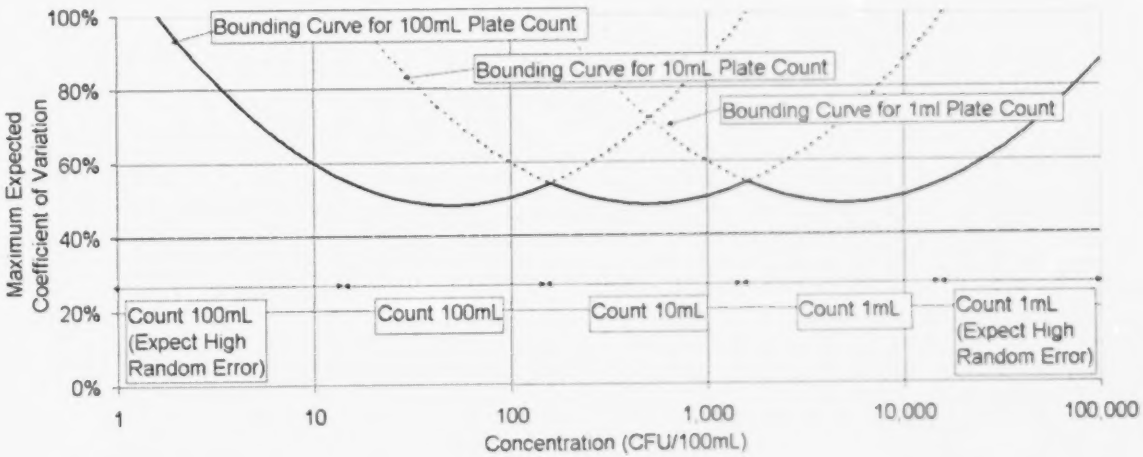

Fig. 7. Minimization of random error in membrane filtration using different sample volumes.

field. This is likely attributable to environmental Gram-negative noncoliform bacteria present in the water sample. Furthermore, the limit of detection is approximately 1,000 CFU/100 mL, and it is therefore recommended that the dipslides not be used as a presence / absence test for the detection of *E. coli* in drinking water since the high limit of detection leaves open the possibility for false negatives within the range of concentrations that can be hazardous to human health. Thus, the SolarCult dipslides are likely not a suitable tool for conducting field water quality testing as part of an evaluation of HWT technology.

Within the context of the implementation of the biosand filter, there are two roles for which the SolarCult dipslide is particularly well suited. The first is that because the dipslide is a self-contained, easy-to-use method of water testing, with no additional equipment required for incubation (particularly in tropical climates; there the ambient temperature is sufficient), it can be readily used by local health and sanitation representatives to provide an initial estimate as to the severity of microbial contamination of a raw water source. The bounding line shown in Fig. 6 suggests that the MacConkey side of the dipslide can provide an estimate of the upper bound of coliform contamination in a water source. Furthermore, the outcome of the test can help in determining what type of intervention is required and the suitability of any particular HWT technology. In particular, *any* growth on the MacConkey side of the dipslide used to test the raw source water indicates that the biosand filter alone is *not* sufficient to provide clean drinking water, as it can reasonably only be expected to provide a reduction of around 2 log units. In this case, the filtered water would still have greater than 10 CFU/100 mL, and some form of additional treatment including disinfection would still be required.

The second role of the dipslides is as a visual aid for the local health and sanitation representatives to engage community members and promote safe water and hygiene practices within the community. The concept of microorganism presence in water and the connection to human health is often a difficult concept for lay persons to understand as it cannot be visualized. The dipslides can be used to visually demonstrate the severity of microbial contamination in water sources, and show the degree to which the water is improved through safe water practices, in a manner that is clearly understood.

Conclusions

This paper presents the evaluation of the field water quality testing methods used in an evaluation of biosand filters, a form of household drinking water technology, in Posoltega, Nicaragua. The major findings are as follows:

- For the microbial concentrations encountered in the field, the MF methods produced useful, enumerable results that permitted the evaluation of the performance of the biosand filters installed in Posoltega, Nicaragua. The low limit of detection on the finished water allowed the identification of the need for additional treatment involving disinfection for the filtered and stored water.
- The average coefficient of variation computed between tests of different volumes of the same water sample was 51% (SD = 35%). There was no statistically significant difference between the laboratory and field data set, suggesting that the study results would not have had any less random error had the water samples been collected and transported to a controlled laboratory facility for testing.
- The maximum expected random error can be minimized by selecting an appropriate sample volume for performing MF, such that the plate count is in the range of approximately 15 to 150 CFU.
- There was poor correlation between the SolarCult dipslide results and the MF results using m-coliBlue24 in the field. However, in lack of other resources, the dipslides can be used as an effective tool for determining an upper bound of coliform contamination in source water. They should not be used as a presence/absence test for drinking water due to the high limit of detection.
- SolarCult dipslides may prove useful as a visual tool for engaging community members, regarding the importance of water quality, in rural and remote parts of the world.

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Stream Chloride Monitoring Program of City of Toronto: Implications of Road Salt Application

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In cold regions, winter road safety is a major challenge for municipalities and provincial highway transportation agencies. Road salt is widely used to improve winter road conditions, but concerns have been raised about the effects of road salts on the environment. This paper describes a water quality monitoring program designed to measure both background chloride concentrations and the effects of road salt application on stream water quality in four watersheds (Humber River, Don River, Highland Creek, and Morningside tributary of Rouge River) located within the City of Toronto boundary. The effect of road salts on stream water quality was evaluated based on chloride concentration because of its conservative nature. A bilinear correlation was developed to transform measured specific conductance levels in stream water to chloride concentrations. There are no Ontario aquatic fresh water quality guidelines for chloride, but chloride concentrations in almost all the monitored streams in Toronto periodically exceeded chronic and acute chloride threshold levels of the United States Environmental Protection Agency. The City of Toronto has been proactive in its efforts to implement management practices to reduce the impact of road salt application on the environment while maintaining safe driving conditions for its road users. Normalized salt application rates in Toronto have been on a gradual declining trend in the last decade from about 0.08 to 0.07 tonnes of salt applied per centimetre of snowfall per kilometre of lane. With public safety in mind, further reductions in salt application rates are being considered to reduce the adverse environmental effects to acceptable limits.

Key words: **road salt, water quality, stormwater, monitoring, management practices**

Introduction

Snow and ice conditions on the road system have a significant impact on public safety, roadway capacity, travel time, and economic costs (Keummel 1992). At present, control of snow and ice on road pavements and sidewalks is generally achieved by the application of de-icers and mechanical ploughing. Four common road salt de-icers (sodium chloride, calcium chloride, magnesium chloride, and potassium chloride, of which sodium chloride is the most predominant) have been used to minimize snow and ice dangers on road pavements and sidewalks. Salt lowers the freezing point of water and the melting action of the salt forms a brine at the ice–pavement interface. Brine prevents water from freezing and bonding to the pavement (Salt Institute 2007). Approximately 5 million tonnes of road salts are applied on roadways in Canada annually (Environment Canada 2004). The City of Toronto has 5,500 km of roads to maintain (City of Toronto 2005) and applies salt on roads and sidewalks during winter to improve transportation safety.

Chlorides from road salts enter streams primarily through surface runoff and groundwater discharge zones (D'Itri 1992; Ramakrishna and Viraraghvan 2005). Both aquatic and terrestrial ecosystems can be adversely affected by exposure to high chloride concentrations associated with the typical use of road salts (U.S. EPA 1988; Novotny et al. 1999; Williams et al. 2000; Environment Canada and Health Canada 2001). Benbow and Merritt (2004) conducted laboratory and field tests to determine the impact of chloride on macroinvertebrates. They concluded that some macroinvertebrates have a high tolerance to road salts but stated other toxic constituents found in road salts can affect tolerance thresholds. Chlorides alter partitioning between adsorbed and dissolved metals thus increasing the concentration of dissolved metals in snowmelt. Aquatic organisms in smaller ponds and streams with lower baseflow are more susceptible to toxicity due to road salts (Marsalek et al. 2000; Marsalek 2003). In 2004, these concerns prompted Environment Canada to issue a Code of Practice for the Environmental Management of Road Salts, designed to optimize salt application and to reduce chloride transfer to the environment. Currently there are no federal or provincial environmental water quality standards or guidelines for chloride levels for fresh water in Ontario. In the United States, toxicity thresholds have been developed for chloride and include a chronic freshwater quality criterion of 230 mg/L, and an acute freshwater quality criterion of 860 mg/L for small stream flow peaks resulting from snowmelt runoff (U.S. EPA 1988).

The persistence of chlorides in the environment does not allow easy treatment of contaminated water; therefore, the current management approach is to develop appropriate practices to optimize salt use under

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given winter snow and ice conditions, while ensuring the maintenance of roadway safety. These management options primarily focus on alternative de-icing chemicals and the way road salts are currently handled, stored, and used (TAC 2003). Although there have been some studies on the utility of alternative de-icing products, including calcium magnesium acetate, their relatively higher costs prevent widespread use (D'Itri 1992). Additional management options include improved storage and handling techniques at salt storage sites to minimize salt loss from storage facilities. In some locations drainage is collected and used in brine production. Road salt management practices such as prewetting and anti-icing have helped to reduce the amount of salts applied. Road weather information systems (RWIS) are increasingly being used to forecast road pavement conditions, thereby optimizing road salt application (Environment Canada 2004).

The City of Toronto has been proactive in its efforts to protect the environment and human health while maintaining safe transportation routes. Since 2001, the City has developed programs to optimize its salt application rates and to implement various best management practices in the storage, handling, and application of road salt. All of the City road salt storage locations are covered. The City of Toronto has employed prewetting since 2003 and uses anti-icing at problematic locations such as bridge decks and steep slopes. The City salt trucks—equipped with electronic spreader controls that are regulated to ground speed—are used to ensure that a consistent amount of salt is applied on pavements and to provide data that permits salt use to be tracked. The City developed a chloride monitoring program with the objective of gathering data to better understand spatial and temporal distribution of chlorides in response to road salt application. Another objective of the monitoring program is to evaluate the effect of recent road salt management practices on reducing chloride transfer to the environment.

The purpose of this paper is to describe the City of Toronto stream chloride monitoring program and to discuss the effect of road salt application on stream water quality. Chloride concentrations among and within streams are compared on an aggregate basis using probability of exceedance graphs. Seasonal and annual comparisons of stream chloride concentrations are also made. The paper also presents results of the statistical analysis of stream chloride concentrations on an event basis. The chloride monitoring data is discussed in the context of current de-icing operations using chloride loads in the streams and road salt application records for the drainage area.

Materials and Methods

Study Area

The City of Toronto stream chloride monitoring program includes four watersheds within the City limits: namely, the Humber River, the Don River, Highland Creek, and the Morningside tributary of the Rouge River. Most of the Highland Creek watershed is located within the City boundary, while the other streams have their headwaters located north of the City outside its boundary. For example, approximately 50% of the Don River watershed and 75% of the Humber River watershed are located outside the City boundary and consist of mainly agricultural areas. Most of the areas located within the City boundary are highly urbanized with a high density of road networks, except for the Rouge River watershed. The proportion of the watershed located within the City and its land use is important to understand the relative contribution of water quality on streams. Main contributors of road salt within the City are the City of Toronto Transportation Services and the Ontario Ministry of Transportation which is responsible for Highway 401. The typical road salt application rate is 0.07 tonnes per lane kilometre (City of Toronto 2005). There is a minor contribution from businesses and residents due to salt application on parking lots and driveways. The monitoring station locations were selected to cover as much of the City as logistically feasible, and to estimate chloride contributions from sources outside the City's control. Locations of the monitoring stations are shown in Fig. 1.

Monitoring Program

The monitoring program was developed to collect continuous chloride data. Granato and Smith (1999) indicated that discrete or composite samples of highway runoff do not adequately represent in-storm water quality fluctuations because continuous records of water stage, specific conductance, pH, and temperature of the runoff show that these properties fluctuate substantially during a storm. The City of Toronto stream chloride monitoring program uses specific conductance, or electrical conductivity (EC), as a surrogate for chloride (Cl^-) concentration, similar to Howard and Haynes (1993) and Granato and Smith (1999). EC was measured hourly using conductivity sensors (Hach model no. 5798A with

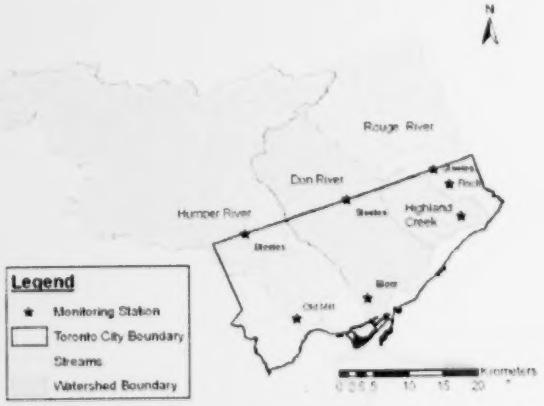

Fig. 1. Monitoring stations location map.

a sensitivity of 0.01 mS/cm) attached to Hach Sigma 900 Max autosamplers.

In addition to the continuous EC measurements, grab sampling was conducted on a regular basis (every 2 to 3 weeks). These samples were analyzed for EC, pH, major ions (sodium, calcium, magnesium, potassium, chloride, sulphate, bromide), nutrients, and metals by the Toronto Water Laboratory. During these site visits, sensors were checked for their performance, and sensor cleaning and recalibration were performed as required.

Data Quality Assurance and Control

Several quality assurance/quality control measures were followed to maintain the accuracy of the data. Sensors fouled without routine maintenance causing lower sensitivity, and as a result, frequent site visits (every 2 to 3 weeks) were required to clean the sensors. Continuous EC data were compared with field EC measurements using a portable EC meter (YSI 30), and with the laboratory results of the grab samples. Compatibility of readings with stream flow, precipitation, temperature, and road salt application data were also checked to identify any anomalies.

Table 1 summarizes the monitoring data availability and drainage area associated with each station. It is noted that there were extended periods without monitoring data from some monitoring stations. This is because the initial interest was mainly on the winter period when road salt application occurs, and then the monitoring program was expanded to collect data year-round to capture all the processes associated with chlorides in the streams. These no-data periods were excluded from the statistical analysis. However, seasonal chloride loads in the streams were estimated only for the periods when continuous data were available.

EC to Cl^- Concentration Correlation

Results from instream grab samples were used to examine the relationship between EC and Cl^- concentration for each stream. There is an overall good linear relationship between EC values and Cl^- concentrations, indicating a dominant effect of Cl^- ions on EC, similar to the Howard and Haynes (1993) and Granato and Smith (1999) results. However, accuracy at lower EC values was poor, as the conversion generated under-estimates of Cl^- concentrations, and occasionally negative values. Impact of other ions (calcium, magnesium, potassium, sulphate) on EC at low Cl^- concentrations was significant, making a simple linear relationship inaccurate. Higher order polynomial equations did not improve the relationship. Accordingly, bilinear equations were developed for all the streams.

A bilinear correlation improved the performance of transformation by removing negative chloride concentrations caused by a single linear relationship. Although low Cl^- concentration values are not critical in assessing the environmental impacts of road salts, they can affect chloride load or annual mass balance calculations. Further refinement of the transformation equation could be achieved by considering the contribution of other ions on EC at low chloride concentrations. Figure 2 presents the bilinear correlation for Highland Creek using analytical results.

Selection of a deflection point of the bilinear graph was determined using a successive approximation approach. The first approximation of the value differentiating high and low values was used to plot the trend lines. The resultant intersection point was used as the next approximation of the deflection point. Successive approximations were carried out until the difference between two successive iterations was not significantly different.

TABLE 1. Monitoring data availability and drainage area by station

Watercourse and station location	*Drainage area (km^2)*	*Data period (data points)*	
Humber River at Steeles	567.4	Dec. 24, 2001 – Sep. 18, 2003	(14,208)
		Dec. 4, 2003 – Sep. 30, 2004	(6,960)
Humber River at Old Mill	877.6	Dec. 24, 2001 – Jun. 17, 2002	(4,195)
		Nov. 6 , 2002 – Jul. 17, 2003	(5,880)
		Oct. 8, 2004 – Jan. 25, 2005	(2,617)
Don River at Steeles	59.5	Oct. 1, 2003 – May 2, 2005	(13,887)
Don River at Bloor	300.6	Jan. 23, 2002 – Jun. 18, 2002	(3,522)
		Nov. 27, 2002 – Aug. 25, 2003	(6,498)
		Oct. 27, 2004 – Apr. 1, 2005	(3,739)
Highland Creek at Morningside Ave.	79.2	Nov. 17, 2004 – Sep. 30, 2007	(25,137)
Morningside tributary at Steeles	8.6	Nov. 27, 2003 – Aug. 22, 2006	(16,604)
Morningside tributary at Finch	14.6	Dec. 2, 2003 – Apr. 11 , 2005	(11,888)
		Aug. 26, 2005 – Nov. 4, 2005	(1,680)
		Jan. 9, 2006 – Sep. 15, 2006	(5,589)

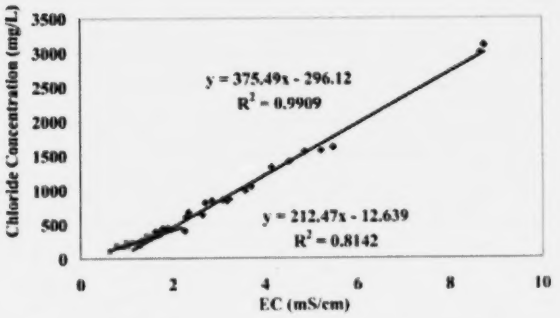

Fig. 2. Correlation between EC and Cl^- concentration—Highland Creek.

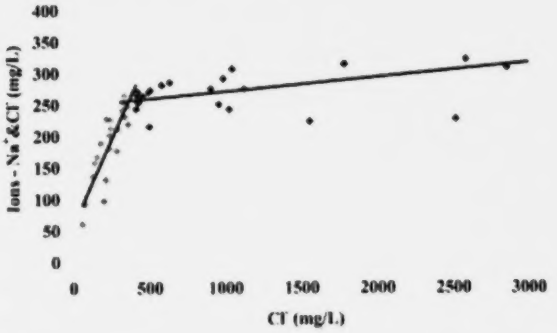

Fig. 3. Comparison between Cl^- concentration and total ions (minus sodium and chloride)—Highland Creek.

Table 2 summarizes the bilinear equations developed to transform EC to Cl^- concentration. It is noted that the deflection point differs from one stream to another and its magnitude is related to the Cl^- concentration values monitored at the stream. The deflection point for Highland Creek is approximately 375 mg/L, and the Morningside tributary has the lowest deflection point of 150 mg/L. Highland Creek, the Don River, and the Humber River had decreasing values in the same trend of background chloride concentrations.

The suitability of the bilinear relationship was tested considering the other major ions in water, except for sodium and chloride. Comparison of chloride ions with other ions except, for sodium and chloride (main constituents of road salts), indicated a very similar deflection point as shown by the EC versus Cl^- relationship. Figure 3 presents the graph of total ions (minus sodium and chloride) versus chloride for grab samples collected from Highland Creek.

Results and Discussion

Hourly EC monitoring data provided a better understanding of spatial and temporal variation of stream chloride concentrations. Calculated chloride concentrations from City of Toronto stream chloride monitoring stations were used for the analyses presented. Although data from all the monitoring stations are presented, data from the Highland Creek station has been given more consideration because the data are uninterrupted and spans for few years. Figure 4 presents a box and whisker plot for aggregate winter (November to March) chloride concentrations in the streams.

The data show that chloride concentrations were highly variable, but the values are similar to those previously reported in the literature (Howard and Haynes 1993; Granato and Smith 1999; Mayer et al. 1999; Novotny et al. 1999). Chloride concentrations ranging from 350 to 3,050 mg/L were measured by Novotny et al. (1999) from a creek in Milwaukee, Wisconsin. They also reported chloride concentrations as high as 17,200 mg/L from a storm sewer in Syracuse, New York. Granato and Smith (1999) reported highway runoff chloride concentrations, which ranged from 10 to 20,000 mg/L in southeastern Massachusetts. Mayer et al. (1999) summarized chloride concentrations reported from Canadian surface waters, and values reported from Ontario and Quebec show similarity to the results from this study.

According to Fig. 4, within the same stream, downstream stations showed higher chloride concentrations when compared with upstream stations, indicating the cumulative impact of increased salt loading due to higher urbanization within the City of Toronto. Highly urbanized drainage areas such as the Highland Creek and Don River watersheds have higher chloride concentrations when compared with less developed areas, such as Morningside Creek.

TABLE 2. Bilinear Equations developed for the streams to transform EC to Cl^- concentration

Watercourse and station location	*Chloride [a] (mg/L)*	*Equation above and below the deflection point (Coefficient of Determination)*
Humber River	200	323.07x – 144.31 (0.9929) 222.76x – 60.286 (0.8178)
Don River	300	345.58x – 205.98 (0.9932) 213.89x – 51.389 (0.8003)
Highland Creek	375	375.49x – 296.12 (0.9909) 212.47x – 12.639 (0.8142)
Morningside tributary	150	307.81x – 144.31 (0.9929) 228.09x – 61.92 (0.8751)

[a] Chloride concentration at deflection point.

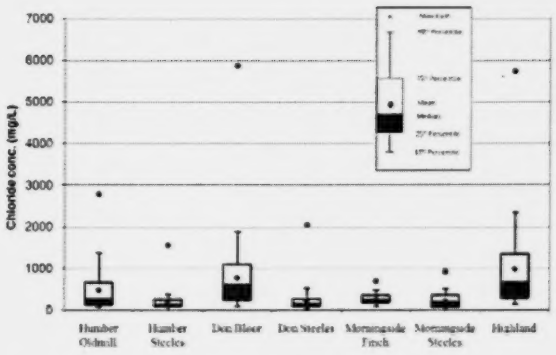

Fig. 4. Statistical summary of chloride concentrations (November to March).

Probability of Exceedance

Probability of exceedance curves were developed for each monitoring station to evaluate the proportion of time stream chloride concentration was above any concentration value. Probability of exceedance for a particular chloride concentration was calculated by dividing the number of hours with a higher value than the chloride concentration by the total number of hours for which data was available.

The probability of exceedance analysis was categorized according to season: November to March, April to June, and July to October. The November to March period includes winter and early spring to account for salt application and spring snow melt. The July to October season predictably showed the least impact from road salt application, and the April to June period was an intermediate season. Figure 5 presents seasonal probability of exceedance of chloride concentrations at the Highland Creek monitoring station.

The contrast in chloride concentrations between the winter period (November to March) and rest of the year is evident from the graph and is similar for all stations. During this period, the chloride concentration at Highland Creek is likely to exceed the United States Environmental Protection Agency (U.S. EPA) criteria of 230 mg/L (chronic threshold) approximately 80% of the time, and the acute threshold is likely to be exceeded 35% of the time. Downstream locations in the Don River also indicate similar exceedances. The Humber River downstream location exceeded the chronic threshold only 35% of the time due to the effect of its less urbanized headwater areas. The Morningside tributary and Humber River upstream stations recorded lowest exceedance probabilities. Most of the literature on urban winter stream water quality (Howard and Haynes 1993; Novotny et al. 1999; Marsalek et al. 2000; Marsalek et al. 2003) indicates frequent exceedance of U.S. EPA criteria for chloride, but there are no recorded quantitative estimates.

Variation in concentrations between upstream and downstream locations of a stream is demonstrated in Fig. 6 by showing winter chloride probability of exceedance values for the Don River monitoring stations. It is noted that the Bloor station is located approximately 20 km downstream of the Steeles station. The higher chloride concentrations in downstream locations could be attributed to higher road density within the City of Toronto.

Year to year variation in probability of exceedance in chloride concentration at a monitoring station provides an indication of the effectiveness of road salt management practices because a reduction in salt use should be accompanied with a decrease in chloride concentrations in the stream. However, it is important to consider theses results in light of any year-to-year change in climatic factors, such as total snowfall and average winter temperature. Available chloride data sets do not span to cover before and after implementation of the City's salt management plan best practices to undertake this analysis. Yearly variation for the Highland Creek November to March chloride concentration is presented in Fig. 7. Year 2004/2005 winter recorded higher stream chloride concentrations compared with other years, mostly due to the relatively high snowfall quantity in that year. Chloride values for winter 2005/2006 and 2006/2007 show similar probabilities of exceedance, but 2006/2007 recorded slightly lower probabilities, especially above 230 mg/L.

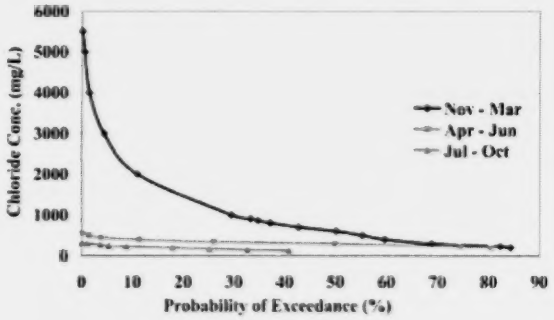

Fig. 5. Seasonal probability of exceedance of chloride for Highland Creek.

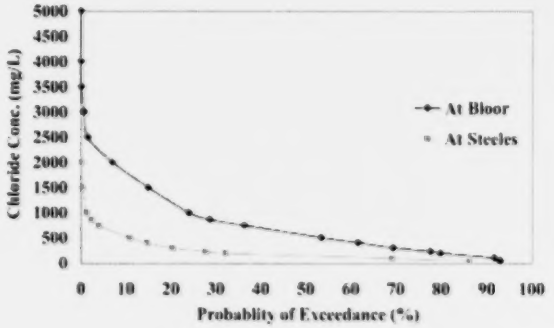

Fig. 6. Probability of exceedance of chloride—Don River (November to March).

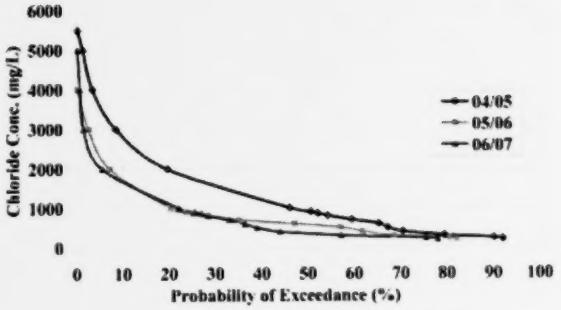

Fig. 7. Annual probablity of exceedance—Highland Creek (November to March).

Chloride Event Statistics

An analysis of the chloride events (based on pollutograph time series) was also undertaken to study the impact of each salt application or precipitation event on chloride concentration in the streams. The chloride events were based on thresholds of 230 and 860 mg/L (representing the chronic and acute chloride levels specified by the U.S. EPA) and an additional threshold, 1,500 mg/L. Figure 8 indicates how the chloride events were defined. Duration and peak chloride concentration were derived from each event.

Subsequent analyses were mainly based on Highland Creek monitoring data. This station was selected mainly because of the availability of continuous data for at least three years. This watershed is also located almost entirely within the City of Toronto, minimizing impacts due to different road salt application and management practices implemented by other jurisdictions. It is noted that the majority of roads in this watershed are maintained by the City of Toronto, except for Highway 401 which is maintained by The Ministry of Transportation, Ontario (MTO).

Table 3 presents the summary of chloride event statistics for the monitoring station at Highland Creek. Any 230 mg/L event less than 3 hours in duration was removed from the analysis to prevent a bias of statistics

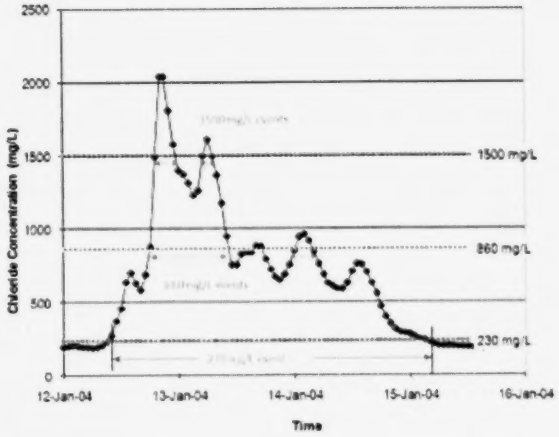

Fig. 8. Determination of chloride events.

towards lower peaks and mean event durations. It was observed that the difference between the peak value and 230 mg/L for these very low-duration events was within the accuracy of the EC sensor.

The results in Table 3 confirm the trends in Fig. 7. Winter period 2004/2005 recorded a higher number of events, total duration of exceedance, and mean event maximum chloride concentration, confirming the fact that winter 2004/2005 was severe with a comparatively high snowfall. Winters 2005/2006 and 2006/2007 have similar characteristics, but 2006/2007 indicated longer mean event durations and fewer events. Standard deviations for both event duration and event maximum concentration showed high variability.

Normalized Road Salt Application Rates

It is important to understand the relationship between stream chloride concentrations and actual road salt application rates. Total amount of road salt applied per year provides a comparative measure to evaluate effectiveness of road salt management practices. The limitation of this method lies in the fact that it does not consider yearly variation in snowfall and other meteorological factors.

TABLE 3. Chloride event statistics for Highland Creek monitoring station

Winter period	*Chloride threshold (mg/L)*	*No. of events*	*Total duration of exceedance (h)*	*Mean event duration (h)*	*Standard deviation (h)*	*Mean event max. conc. (mg/L)*	*Standard deviation (mg/L)*
2004/05	230	33	5,253	164	±257	974	±1,640
	860	19	1,682	88	±113	2,500	±1,689
	1,500	22	1,025	47	±58	2,674	±1,429
2005/06	230	32	4,522	141	±203	815	±1,254
	860	23	915	40	±60	1,834	±1,180
	1,500	12	427	36	±33	2,638	±1,154
2006/07	230	20	3,796	190	±165	820	±1,226
	860	9	754	84	±59	2,148	±1,253
	1,500	8	348	44	±44	2,433	±1,173

Normalizing the road salt application rate by cumulative snowfall and total length of roadway lanes provides a better comparative tool for the purpose of evaluating road salt related best management practices. The normalized application rate accounts for the main factor affecting road salt application, cumulative snowfall, and also allows comparison between different areas or jurisdictions because it considers the total length of road network.

Table 4 presents calculated normalized road salt application rates used by the City of Toronto. Road salt used by MTO, City residents, and businesses are not included. The nearby Environment Canada weather station in North York was used to obtain snowfall accumulation data. Although there is considerable variation, these values are consistent with the specified road salt application rates in North America (City of Toronto 2005; Salt Institute 2007) for road safety. The variability indicates that there are other factors, other than total annual snowfall, that affect road salt application rates. It also indicates that there is a potential to optimize the application rates to minimize adverse environmental effects. Figure 9 graphically presents the normalized road salt application rates shown in Table 4 for better visualization.

Normalized road salt application rates based on snowfall and total lane kilometres show some year-to-year variation, but with a declining trend over the last 10 to 12 years. On average, the normalized salt application rate for the City of Toronto has been reduced from 0.08 tonnes per cm of snowfall per lane kilometre to 0.07 tonnes per cm of snowfall per lane kilometre during this period.

Additionally, the normalized road salt application rates were determined for the Highland Creek watershed considering both City and MTO application data. Table 5 presents calculated normalized road salt application rates used in the Highland Creek watershed by the City and the MTO. These data show that very similar application rates were used within the last five years; however, it was difficult to come to any conclusion regarding the

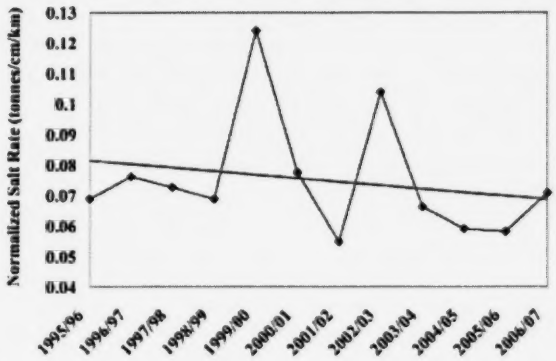

Fig. 9. Normalized salt application rates for the City of Toronto.

effectiveness of salt management practices implemented by the City by only considering normalized application rates. A closer look at the methodology indicates that this method does not account for all the factors that affect road salt application. For example, the amount of salt required to melt the same amount of snow varies with temperature, with low temperatures requiring more road salt (TAC 2003). Snow clearing policies also have an impact on the amount of salt applied. For example, if a large amount of snow fell within a short time period, the majority of it would be ploughed and possibly removed resulting in a lower amount of road salt being applied. However, if an equivalent amount of snowfall was received over a prolonged single storm, or a series of successive smaller storms, road salt would be applied several times resulting in a higher application ratio. Also, if very small quantities of snow were to fall during above-zero temperature conditions, then the snow would likely melt and may require little to no road salt. Possible spatial variation of snowfall within the watershed would also introduce errors. Another factor affecting road salt application rate is the form of precipitation. For example, during freezing rain events, the only effective control measure is the application of de-icing chemicals;

TABLE 4. Normalized road salt application rates — City of Toronto

Winter period	*Total amount of road salt applied (tonnes)*	*Cumulative snowfall (cm)*	*Length of roadway lanes (km)*	*Normalized road salt Application (tonnes/cm/km)*
1995/06	127,977	150.4	12,343	0.069
1996/97	157,585	166.6	12,415	0.076
1997/98	101,939	112.2	12,493	0.073
1998/99	140,410	124.0	12,493	0.069
1999/00	142,869	88.4	13,846	0.124
2000/01	176,595	181.2	13,800	0.078
2001/02	56,893	77.4	13,800	0.055
2002/03	208,230	145.2	13,800	0.104
2003/04	108,152	108.2	15,052	0.066
2004/05	147,433	165.5	15,052	0.059
2005/06	94,673	108.1	15,052	0.058
2006/07	89,112	83.4	15,052	0.071

TABLE 5. Normalized road salt application rates—Highland Creek

Winter period	*Total amount of road salt applied (tonnes)*	*Cumulative annual snowfall (cm)*	*Length of roadway lanes (km)*	*Normalized road salt Application (tonnes/cm/km)*
2002/03	22,019	145.2	1,263	0.12
2003/04	14,783	108.2	1,377	0.099
2004/05	20,673	165.5	1,377	0.091
2005/06	14,628	108.1	1,377	0.098
2006/07	12,654	83.4	1,377	0.11

therefore, normalizing salt application by total snowfall is not always a correct indicator, although it provides a comparative tool. Table 6 summarizes the parameters affecting road salt application for the period of 2001 to 2007, which can be used to further analyze application rates. The meteorological data was obtained from the North York Environment Canada weather station.

Information in Table 6 provides a better picture of the factors affecting road salt application. For example, in 2001/2002 it was a relatively warmer winter and this resulted in a lesser amount of road salt applied (refer to Fig. 9). The data also indicate that although 2006/2007 had less total snowfall and fewer number of days with snow, lower mean temperatures required more road salt application when compared with 2005/2006.

Instream Chloride Loads

Chloride load (mass) within the streams can also be used to determine effectiveness of management practices employed by the City since it indicates how much road salt is applied in the drainage area. Monitoring chloride concentration and the corresponding stream flow rate provides a means of achieving this quantity. Hourly data at a minimum is required for accuracy of the chloride load estimates since chloride concentrations can vary significantly within several hours. The Highland Creek monitoring data (which is the most complete data set), however, do not permit comparison of chloride load prior to and after implementation of best management practices, since data acquisition started in 2004.

Chloride load is calculated by multiplying chloride concentration by the flow rate. Contribution of chloride mass due to baseflow should be accounted for accurate estimates of chloride load due to road salt application. Considering the daily stream flow values (Water Survey Canada flow data), baseflows were determined using the digital filter developed by Arnold and Allen (1999). Chloride concentration under baseflow conditions were determined to be approximately 200 mg/L based on stream chloride concentrations during dry periods in the summer.

Figure 10 presents the instream chloride load resulting from road de-icing operations within the Highland Creek watershed. The instream chloride mass indicates an increase of salt in the stream within the winter period, and a drastic drop in the summer, with the lowest levels occurring in the fall. This pattern was previously identified by Howard and Haynes (1993). It is apparent that there was a continued reduction in chloride mass in Highland Creek during winters ranging from 2004 to 2007. The reduction in chloride mass is partly due to lower amounts of snowfall and could also indicate the effect of best management practices.

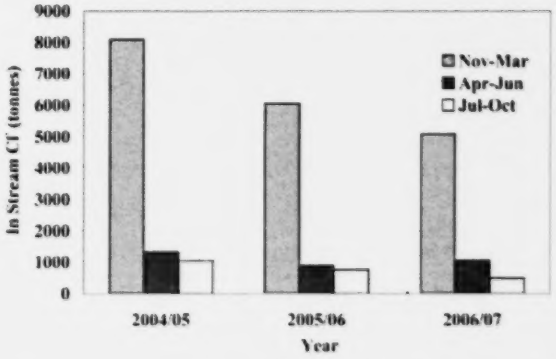

Fig. 10. Variation of seasonal instream chloride load in Highland Creek.

TABLE 6. Meteorological parameters affecting road salt application

Winter period	*Days >2 cm of snowfall*	*Days <0 °C after precipitation*	*Days >10 cm of snowfall*	*Mean winter daily max temp (°C)*	*Winter daily mean temp (°C)*
2001/02	13	5	3	3.1	-0.6
2002/03	19	18	4	0.3	-3.8
2003/04	17	15	0	0.7	-3.3
2004/05	23	15	3	0.7	-3.5
2005/06	16	7	1	1.72	-1.8
2006/07	9	9	1	0.9	-2.8

Conclusions

The analysis of chloride concentration data from eight monitoring stations in four Toronto streams (Humber River, Don River, Highland Creek, and Morningside tributary in the Rouge River) indicated elevated chloride concentrations during winter months. The Highland Creek monitoring station exceeded the U.S. EPA chronic chloride limit about 80% of the time during the winter, and the acute limit was likely exceeded approximately 35% of the time during the monitoring period. The effect of relative urbanization of each watershed was also noticeable; the Humber River with a relatively large nonurbanized drainage area exceeded the chronic limit approximately 25% of the time.

It was also found that the majority of road salt applied runs off to the streams in a watershed during winter and early spring, with a smaller quantity continuing to discharge during the rest of the year. Stream chloride concentration and load depend on several factors, including total amount of snowfall and type of precipitation, average winter temperature, and also road salt application rate and the management practices implemented. However, available monitoring data is insufficient to make a concrete conclusion on the effectiveness of road salt management practices implemented by the City of Toronto due to the limited span of data.

Normalized salt application rates in Toronto have been on a gradual declining trend in the last decade, from about 0.08 to 0.07 tonnes of salt applied per centimetre of snowfall per lane kilometre. Further reductions in salt application rates should be explored in order to reduce adverse environmental effects to acceptable limits.

Acknowledgments

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Environmental Factors Affecting Methoprene Concentrations for West Nile Virus Control in a Storm Sewer System

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To address vector-borne West Nile virus in Canada, chemical larvicides (methoprene) are applied to storm sewer system catch basins (CBs) to control mosquitoes. This study assessed the fate and transport of methoprene in such systems over time relative to precipitation. Rainfall and methoprene concentration patterns revealed the effect of dilution, dissolution, and flushing of the larvicide. In the summer and fall of 2003 to 2005, field monitoring studies were conducted in Toronto, Ontario on two CBs, each treated with a control dose of methoprene, supplied in pellet or ingot formulation. Furthermore, in 2005, concentrations at the storm sewer outfall were measured during nine rainfall events. Based on daily monitoring, findings indicate that (1) the methoprene concentration at the CBs fell below the minimum lethal concentration or LC_{50} one or two weeks after treatment, and remained below LC_{50} concentrations over 70% of the time; (2) rainfall flushed methoprene from the CBs to the storm sewer outfall at concentrations higher than the levels specified by Ministry of Environment, which may cause ecosystem damage; (3) based on the number of cycles per diem within each CB in each study period, there was no conclusive pattern in the flushing susceptibility of pellets versus ingots; (4) the mean concentration of methoprene increased with reduced CB sump volume; (5) less total precipitation resulted in higher average methoprene concentrations and a higher number of days above the LC_{50} based on ingot-dosed CBs; (6) counter-intuitive to (4) and (5), larger sump water volumes and greater rainfall resulted in lower mean concentrations and fewer days above the LC_{50}; and (7) a single ingot dosage was comparable in performance to a three pellet dosage.

Key words: West Nile virus, methoprene, larvicides, rainfall

Introduction

The West Nile virus, transmitted to humans by mosquitoes, is established in Ontario, Canada (MOHLTC 2008). According to the City of Toronto, 98 humans tested positive for West Nile virus between 2003 and 2007 (Toronto Public Health 2007). Catch basins (CBs) were identified as being important breeding grounds of mosquitoes, and in Toronto it was confirmed that mosquito larvae of species likely to carry West Nile virus were present in most CBs sampled (City of Toronto 2008). The decision to larvicide CBs in the city was due to the large number of reported cases of infections in 2002. Since the larviciding programs in 2003, the number of reported infections have dropped significantly.

The City of Toronto undertook larviciding programs to control mosquitoes in the summer months of 2003 to 2005 during the peak reproduction cycle of *Culex pipiens*. In 2005 a total of 197,052 CBs were treated. The larvicide, methoprene, commercially known as Altosid in pellet formulation, Registration #21809 under the *Pest Control Products Act*, Canada, contains approximately 4.25% active ingredient. The ingot is a slow release formulation. Methoprene (isopropyl-11-methoxy-3,7,11-trimethyl-2-4-dodecadienoate) kills mosquitoes by preventing the natural maturation of larvae, and has a LC_{50} of 0.3 to 2.3 µg/L for *Culex pipiens* (Amin and White 1984; Ali et al. 1995). Methoprene is considered by the U.S. Environmental Protection Agency (U.S. EPA) as a 'least toxic' insecticide (U.S. EPA 2000). Spiegel and Novak (1999) found that methoprene was effective in Illinois CBs for one month, despite physical variations and differing water depth in the CBs.

The fate and transport of methoprene formulations from stormwater sewer systems to watersheds in Canada is largely unknown. In 2003, Struger et al. (2007) conducted a field study on the occurrence and fate of methoprene and its metabolites in CBs and receiving water in Hamilton Harbour and Cootes Paradise in Ontario. They concluded that dissolved methoprene and its derivatives are quickly flushed from CBs during rainfall events. However, concentrations at the outfalls fell quickly and were mostly undetectable in the receiving waters. The half-life of methoprene in the environment is four weeks for hydrolysis, 10 hours for photolysis, and 10 days in soil, and its water solubility is <200 µg/L (Wellmark International 2004). Although methoprene toxicity to fish is low (LC_{50} for bluegill trout is 760 µg/L), levels in excess of 10 µg/L could have detrimental effects on nontarget invertebrates that are important sources of food for fish (Ross et al. 1994). Fish and frog deformities may be attributed to the metabolite methoprenoic acid, which mimics retinoic acid (Kleiner 1997; LaClair et al. 1998; Sea Technology 1999). Methoprene and its

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metabolites may also have unknown effects downstream from where it is applied.

Former research at Ryerson University has evaluated methoprene concentrations relative to rainfall and CB sump volumes within three discrete periods in 2003 to 2005. This paper presents the fate of methoprene at the CBs and the storm sewer outfall, and a multidimensional factor analysis of methoprene concentrations with respect to the methoprene formulation (i.e., ingot versus pellet), water levels at the CBs, and rainfall over the three years. To our knowledge, this is the first multiyear analysis of the fate, transport, and critical environmental factors affecting methoprene in a storm sewer system in North America. It is hoped that the findings may improve program efficacy and cost-effectiveness for reducing human infection rates of West Nile virus while balancing negative ecological impacts. The scope of the research was limited to field study monitoring and water sample analysis.

Methods

Field Study Method

The study site consisted of two CBs on Silverview Drive near the intersection of Willowdale Avenue within the Newtonbrook sewershed in Toronto. The streets service medium- to low-density residential land that includes trees and lawns. One of the CBs is shallow (11.5-cm sump water depth) and the other deep (106-cm sump water depth). The storm sewer outfall is 50 m southeast of the Willowdale Avenue / Silverview Drive Intersection, and becomes the origin of Newtonbrook Creek which joins the East Don River. The East Don River is part of the Don River, which flows into Lake Ontario via the Toronto Harbour. The storm sewer system drains an approximately 360 hectare basin.

In 2003, three separate gauges recorded rainfall data: Earl Bales station at Bathurst Street and Sheppard Avenue (approximately 3.75 km to the southwest); Mitchell field station at Church Avenue (approximately 1.13 km to the south); and a local station at Willowdale Avenue and Silverview Drive to the northeast. In 2004 and 2005, precipitation records used in the assessment came solely from the local gauge operating within the monitoring site. Through a field monitoring program, larvicide dosages were applied either as pellets (0.7g per CB) or a single ingot (45.33g per CB) as per Table 1.

TABLE 1. Methoprene dosage log

Formulation	*Year*	*Date (day-month)*	*Shallow CB*	*Deep CB*
pellet	2003	4-July	1	1
		9-August	1	1
		9-September	1	1
ingot	2004	16-July	1	1
ingot	2005	2-July	1	1

Methoprene prevents emergence from the pupal stage with no effect on larvae. Altosid cylindrical pellets or chalk-like ingots are designed to inhibit mosquito emergence and be effective for up to 30 or 120 days, respectively, according to the manufacturer and field trials by Floore et al. (1991) and Spiegel and Novak (1999). Water was sampled daily from each CB using a small mechanical pump fitted with a long stainless steel tube. The outfall water was sampled during study-period rain events in 2003 to 2005 using an automatic wastewater sampler. Daily water samples were analyzed by the City of Toronto's Wastewater Laboratory for methoprene using the United States Geological Survey method of liquid-liquid extraction, and gas chromatography/mass spectrometry (GC/MS) (Zimmerman et al. 2001). The United States Geological Survey's method of analysis and quality assurance practice were developed for the determination of four mosquito insecticides (malathion, methoprene, phenothrin, and resmethrin) and one synergist (piperonyl butoxide) in water. The analytical method requires liquid-liquid extraction and GC/MS. Water samples were collected in glass-fibre bottles. At the laboratory, each bottle was assigned an identification number. A surrogate compound was added and a small volume of sample was removed from the bottle; the remaining sample in the bottle was mixed with hexane. The hexane extract was then removed and evaporated under nitrogen within the internal standard. The sample components were separated, identified, and measured by injecting an aliquot of the concentrated extract into a high-resolution, fused-silica capillary column of a GC/MS system under selected-ion mode (SIM). The compounds eluted from the GC column were subsequently identified by comparing their measured ions and retention times with the reference ions and retention times obtained by the measurement of control standards under the same conditions used for the water samples. The concentration of each identified compound was measured by assessing the mass spectrophotometer response of the quantitation ion produced by each compound in relation to the mass spectrophotometer response of the quantitation produced by the surrogate standard. The United States Geological Survey method detection limit ranged from 0.02 to 0.05 µg/L. The recovery factor for the methoprene ranged from 0.56 to 0.58.

Method of Analysis

Using the primary data collected from the field study, multidimensional factor comparisons were made through descriptive indicators that used basic statistical measures such as mean, standard deviation, percentage, and relative frequency. In Table 2, the indicators are grouped into the following categories: overall study; yearly overall; CB versus yearly; and CB overall. Notations below Table 2 define yearly rainfall and less obvious indicators.

A residual concentration spike which returns to a baseline value is considered a cycle. The multidimensional comparisons made in the next section include: overall dry versus wet weather years; deep versus shallow CBs; deep

versus shallow CBs in dry versus wet ingot dosage years; and pellet versus ingot formulations in maintaining LC_{50}. In this manner, the general relationships and patterns between the factors of precipitation, CB sump volume, and methoprene formulation and concentrations are empirically described across the three study periods to aid in improving treatment efficiency. With these relationships and patterns highlighted, continued and refined field monitoring are needed to develop a more robust dataset to enable statistical analysis to be performed. Such analysis can ascertain if statistically valid correlations exist between those factors which can then be deemed most pertinent to improving the effectiveness of West Nile virus treatment programs.

TABLE 2. Methoprene monitoring results of CBs within study period in a letter by number matrix [a]

		1	2	3	4	5	6
	Year (rainfall): [b]	*2003 (wet)*		*2004 (dry)*		*2005 (wettest)*	
	Sump water depth :	*Shallow*	*Deep*	*Shallow*	*Deep*	*Shallow*	*Deep*
OVERALL STUDY							
A	No. of study days	96	96	100.6	100.6	88.7	88.7
B	No. of doses	3	3	1	1	1	1
C	Dosage formulation (0.7g/CB)	Pellet	Pellet	Ingot	Ingot	Ingot	Ingot
D [c]	Mean precip./diem (mm)	2.7		1.5		2.8	
E	No. of rainfall events > 5mm	13		8		14	
YEARLY OVERALL							
F	% of sample dates > LC_{50}/year	12		22		8	
G	Mean meth. conc./year (µg/L)	0.29		0.28		0.19	
H	SD of meth. conc./year	1.41		0.47		0.74	
CB VS YEARLY							
I [d]	% of cycles > LC_{50}/CB/year	75	0	64	50	50	33
J [e]	% of sample dates > LC_{50}/CB/year	24	0	17	28	13	4
K [f]	Mean meth. conc./CB/year (µg/L)	0.55	0.03	0.23	0.31	0.33	0.05
L	SD of meth. conc./CB/year (µg/L)	1.97	0.01	0.43	0.49	1.02	0.1
M	Range of meth. conc. (µg/L)	0.03–15.00	0.03–0.14	0.03–0.60	0.03–3.00	0.00–6.00	0.00–0.51
N [g]	No. of cycles/diem	0.13	0.04	0.11	0.12	0.07	0.07
CB OVERALL			*Shallow CB*			*Deep CB*	
O [h]	3-year mean of peak meth. conc./CB (µg/L)		7.87			1.22	
P [i]	Mean no. of cycles/diem/CB		0.1			0.08	
Q	Mean meth. conc. /CB (µg/L)		0.39			0.13	
R	SD of meth. conc./CB (µg/L)		1.38			0.31	
S [k]	Absolute mean conc. dif. (deep vs shallow CB/year) (µg/L)		Year 2003 = 0.08			Year 2005 = 0.28	
T [m]	Absolute mean conc. dif. (from 2004–2005/CB) (µg/L)		0.10			0.26	

[a] Abbreviations and acronyms: CB = catch basin; No. = number; precip. = precipitation; meth. = methoprene; conc. = concentration; SD = standard deviation; vs = versus.

[b] Rainfall in years 2003, 2004, and 2005 was 238.8 mm (wet), 143.2mm (dry), and 253.3 mm (wettest), respectively.

[c] Mean precip./diem (mm) = average rainfall per day .

[d] % of cycles > LC_{50}/CB/year = percentage of cycles which exceed LC_{50} concentration per catch basin per year.

[e] % of sample dates > LC_{50}/year = percentage of entire catch basin sump water sample dates that exceed LC_{50} concentration in a study year's peri od.

[f] Mean meth. conc./CB/year = average methoprene concentration per catch basin per year.

[g] No. of cycles/diem = average number of cycles per day.

[h] 3-year mean of peak meth. conc./CB = average of peak methoprene concentration over 3 study period years per catch basin.

[i] Mean no. of cycles/diem/CB = average number of cycles per day per catch basin.

[k] Absolute mean conc. dif. (deep versus shallow CB/year) = cell (K,3) – cell (K, 4) versus cell (K,5) – cell (K,6).

[m] Absolute mean conc. dif. (from 2004–2005/CB) = cell (K,5) – cell (K,3) versus cell (K,6) – (K, 4).

Results and Discussion

Catch Basin Results

Results are summarized and referred to in Table 2 using row identifiers. Study years are classified as wet or dry noting a benchmark average annual rainfall in Toronto, Ontario, Canada at the Downsview station, 6158443 (Adams and Papa 2000). Normalized to 88.7 days (the minimum study period), the station's average annual rainfall was 140.5 mm [(average volume/event (4.7mm) x average number of events (93.3)] at an inter-event time definition of 2 hours. Inter-event time definition is the minimum temporal spacing without rainfall to consider two rainfalls as belonging to different events for statistical analysis.

General trends. In general, within both CBs, rainfall diluted and flushed the methoprene, resulting in residual concentrations below the LC_{50} (0.3 µg/L) over 70% of the time. The highest percentage of sample dates exceeding the LC_{50} (28%) occurred in the dry year 2004 within the deep CB (row J, Table 2). The overall pattern observed was a concentration peak above the LC_{50} after the initial dosage, a flush and/or dilution during heavy rainfalls, and a slow recovery with a peak again (Fig. 1–5). Residual concentration spikes that return to a baseline value are considered cycles. In this study, such a cycle caused by a rainfall event was considered an indicator of a flushing event. The frequency of cycles tended to decrease over time as the formulation was dissolved, diluted, degraded, and flushed. During some extended dry weather periods, concentrations did peak above initial dosage concentrations over three- to five-day periods within the deep CB in 2004 and 2005 (Fig. 3 and 5). This may be due to the ingot's slow-release formulation. Sump temperatures in the CBs were stable and permissive for mosquito reproduction at around 18.0 to 25°C throughout the study periods. Results were further analyzed below by the multidimensional comparisons.

Dry versus wet weather—ingot dosage study years. As indicated in Table 2, less precipitation across both basins resulted in a higher percentage of sample dates with concentrations above the LC_{50} (row F), and a higher mean concentration of methoprene (row G). Overall, this was likely caused by less volumetric dilution within the

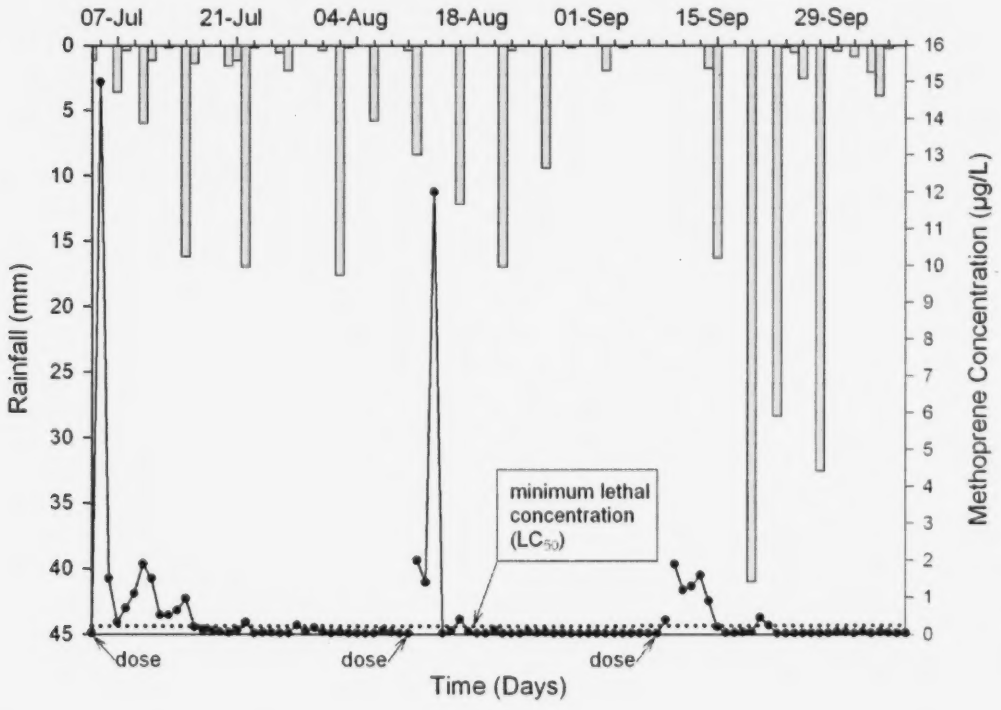

Fig. 1. Hydrodynamics of a three-pellet methoprene dosage (application time indicated as "dose") at the shallow catch basin in 2003; rainfall represented as bars from the top, and methoprene concentration as discrete points joined by a line after dosage points; the disconnections of plotted points are associated with missing data.

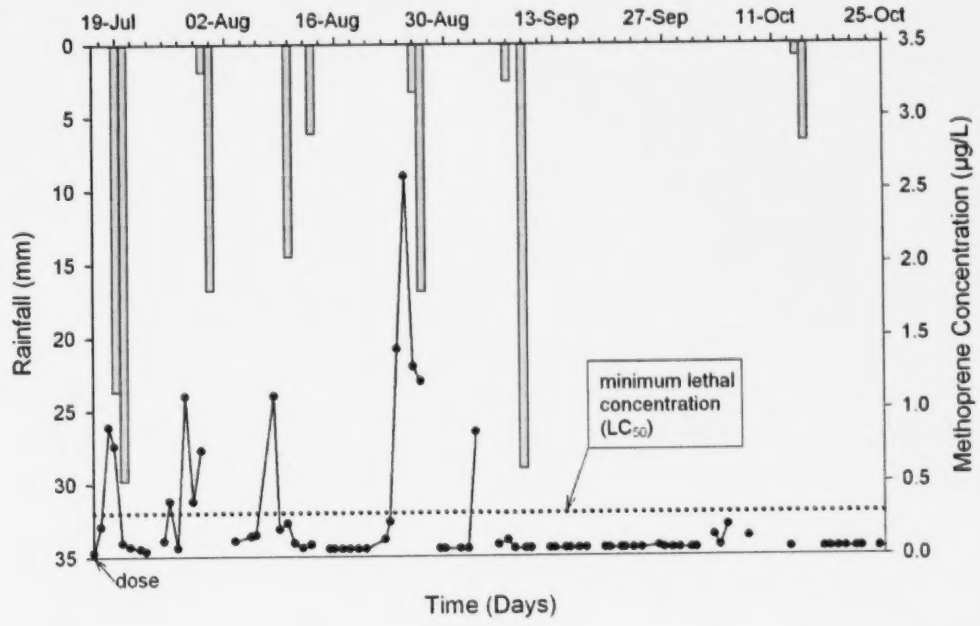

Fig. 2. Hydrodynamics of a single-ingot methoprene dosage (application time indicated as "dose") at the shallow catch basin in 2004; rainfall represented as bars from the top, and methoprene concentration as discrete points, some connected by a line; the disconnections of plotted points are associated with missing data.

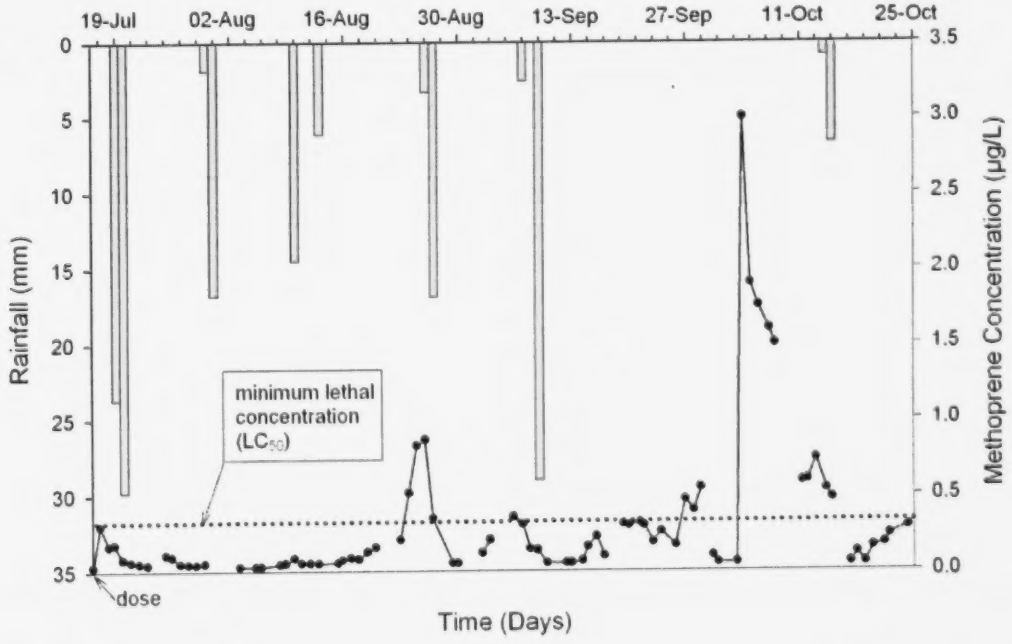

Fig. 3. Hydrodynamics of a single-ingot methoprene dosage (application time indicated as "dose") at the deep catch basin in 2004; rainfall represented as bars from the top, and methoprene concentration as discrete points, some connected by a line; the disconnections of plotted points are associated with missing data.

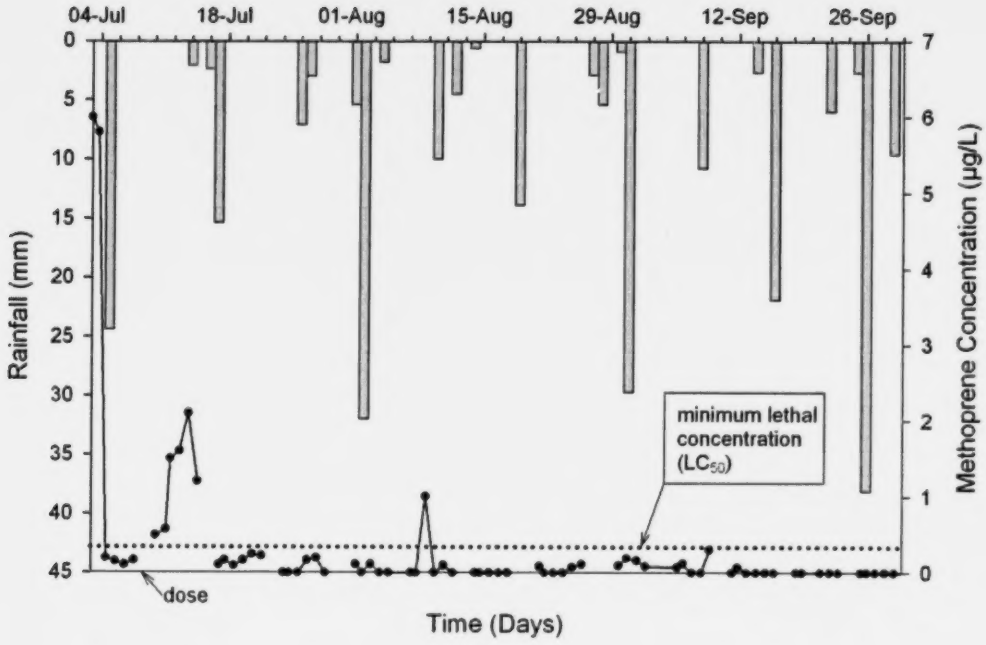

Fig. 4. Hydrodynamics of a single-ingot methoprene dosage (application time indicated as "dose") at the shallow catch basin in 2005; rainfall represented as bars from the top, and methoprene concentration as discrete points, some connected by a line; the disconnections of plotted points are associated with missing data.

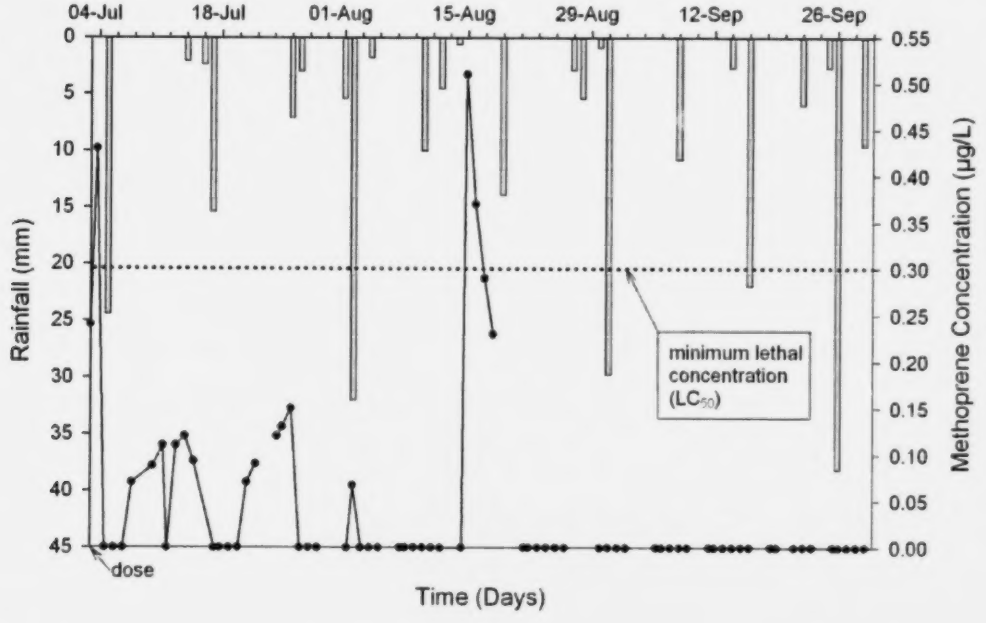

Fig. 5. Hydrodynamics of a single-ingot methoprene dosage (application time indicated as "dose") at the deep catch basin in 2005; rainfall represented as bars from the top, and methoprene concentration as discrete points, some connected by a line; the disconnections of plotted points are associated with missing data.

CBs, associated with a lower number of rainfall events (row E) and mean precipitation/diem (row D). Flushing (represented by the number of cycles per diem within each CB over the three study periods [row N]) displayed no identifiable pattern, and the mean number of cycles/diem/CB were separated by a value of 0.02 (row P) in the deep versus shallow CB.

Deep versus shallow CB—overall. In all study years, the shallow CB compared with the deep CB was subject to a higher percentage of cycles that had concentrations above the LC_{50} (row J) and the mean concentration (row Q). Based on this data, we concluded that as the CB sump water depth increased, the mean concentration of methoprene and the percentage of cycles that had concentrations above the LC_{50} were reduced. This relationship may be due to reduced volumetric dilution and not necessarily flushing based on cycling observations noted in Fig. 1 to 5.

Deep versus shallow CB—dry versus wet study periods using ingots. Based on the two relationships, established above, between rainfall and concentration and CB sump water depth and concentration, it would be expected that the shallow CB compared with the deep CB would achieve, in dry years, higher mean methoprene concentrations and a higher percentage of sample dates with levels over the LC_{50}, and lower concentrations and percentage in the wet year. However, for the dry year (2004), the deep CB had a higher percentage of sample dates with concentrations over the LC_{50} (row J), and higher mean (row K) and peak (row M) methoprene concentrations compared with the shallow CB. In the wet year (2005), the shallow CB exhibited higher values, notwithstanding a short-term methoprene concentration response to the hydrodynamic characteristics of the deep and shallow CBs, as evident in Fig. 1 to 6. In 2003 (the other wet year), pellet dosages in the shallow CB versus the deep CB also exhibited similar results (row J; row K; and row M). Accordingly, it appears that as sump volume and rainfall increase, the mean concentration and days with concentrations above the LC_{50} decrease. These observations hint that methoprene in the shallow CB may be subject to an elevated degradation, perhaps due to (1) elevated biological activity associated with higher temperatures and less dilution, and (2) elevated photolytic degradation since light penetrates more readily through lower sump water volumes.

It is hypothesized that in a dry year, these factors seem to operate at a lesser rate than the effects of dilution in a wet year. The difference between the mean concentrations in the shallow and deep basins in the dry year (2004) is lower than that of the wet year (2005) at 0.08 µg/L versus 0.28 µg/L (Row S), respectively. Comparing the absolute change in concentration within the CBs from 2004 to 2005 (at 0.10 µg/L [shallow CB] versus 0.26 µg/L [Row T]) also lends evidence to this hypothesis. The deeper basin, aside from greater volumetric dilution, may be less susceptible to these degradation factors during the same dry period due to protection offered by a greater sump water volume. However, in a wet year, dilution rates were higher and may have had more effect upon the deeper basin. Dilution rates appear to have more effect on methoprene concentration than the rate of microbial and/or photolytic breakdown in a dry year. Further study that examines in situ sump water levels, temperature, rainfall, microbial activity, and photolytic degradation relative to methoprene concentrations may shed light on this phenomenon.

Ingots versus pellets in both CBs under similar rainfall. In the wet years of 2003 and 2005 (which exhibited similar mean annual volume and number of rainfall events), ingots appeared to be less prone than pellets to flushing, noting a mean number of cycles/diem to be 0.07, whereas pellets averaged 0.09 (row N, Table 2). Pellets had the highest susceptibility to flushing in wet years with lower sump water volumes (row N). Ingots exhibited a higher mean percentage of cycles with concentrations over the LC_{50} (derived from cell I, 5 – 6; and cell I, 1 – 2), notably due to increases observed within the deep CB. Nonetheless, in both CBs pellets do exceed ingots for the percentage of sample dates with concentrations over the LC_{50} (row F) and the mean methoprene concentration (row G) both by magnitudes of 1.5. Presumably, methoprene from a single ingot dosage is subject to increased photolytic, hydrolytic, and/or microbial degradation sitting in a CB sump, more so than a three-dosage pellet regime. Taken together, the data above indicate there is no substantive difference in performance between pellets and ingots. The result may be greater cost-effectiveness of a single ingot dosage regime in a given jurisdiction, acknowledging other cost factors such as labour.

Referring to Fig. 1 and 6, in 2003, rainfall data emanated from gauges outside of the sampling site. This may explain why the small methoprene peaks did not correspond well with rainfall events. After the rain gauge was installed in the monitoring site in 2004, the inverse correlation between rain events and residual methoprene concentrations became more readily observed (i.e., days 2, 10, and 15 in Fig. 2).

In the deep CB (Fig. 3 and 5), methoprene concentrations peaked immediately after ingot application, and quickly fell below the LC_{50} and remained there except for the occasional one or two peaks. In 2004, residual concentrations were above the LC_{50} for 12 days. The drier season resulted in higher overall concentrations. However, in 2003 and 2005, the wet study years, the deep CB maintained very few sampling dates at or above LC_{50} concentrations.

Sewer Outfall Results

During the 2003 to 2005 study period, the storm sewer outfall was sampled during discrete rain events over the course of the field study (Fig. 7). Each study period exhibited

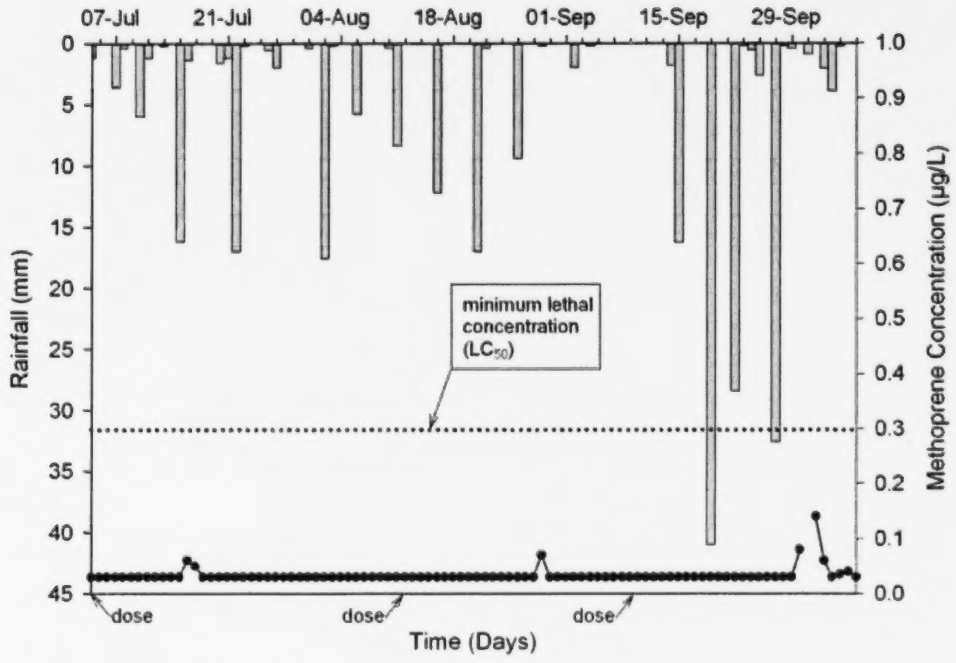

Fig. 6. Hydrodynamics of a three-pellet methoprene dosage (application time indicated as "dose") at the deep catch basin in 2003; rainfall represented as bars from the top, and methoprene concentration as discrete points, some connected by a line; the disconnections of plotted points are associated with missing data.

similar concentration to rainfall patterns. Accordingly, for brevity, 2005 has been selected as a representative year to review. The highest methoprene concentration observed in the outfall (1.20 µg/L) was below the U.S. EPA recommended environmental concentration (10 µg/L) and the ecotoxicity value for aquatic invertebrates (360 µg/L) (U.S. EPA 2001). However, this value was above the temporary Interim Provincial Water Quality Objective (IPWQO) concentration of 0.2 µg/L (MOE 2005), which is 50 times lower than the U.S. EPA concentration limit. Five out of nine water samples taken at the outfall exceeded the IPWQO.

Conclusions and Recommendations

The presence of mosquito larvae was observed in all CBs over the course of the study. Due to the statistically insufficient number of late third and fourth instar larvae present in the collected samples, no efficacy statements can be made at this time.

This field study demonstrated that key environmental and hydrodynamic factors affecting the methoprene concentration in CBs are rainfall and sump water volume. Rainfall affects the residual concentrations by diluting dissolved methoprene from the pellets or ingots. Higher total rainfall in a given season accelerates the dilutive process thereby reducing overall methoprene concentration in CBs, and increasing the influx of methoprene to the receiving waterbody through the storm sewer system. Methoprene concentrations at the sewer outfall during rain events never exceeded the U.S. EPA's limit, yet frequently exceeded the IPWQO. Cumulative impacts to water bodies and biota from methoprene metabolites originating from catch basin treatment requires further research.

Greater sump water volumes appeared to increase the methoprene dilution. Methoprene achieved a higher mean concentration and a greater number of days with concentrations above the LC_{50} in the reduced sump water volume of the shallower CBs. Intuitively, one may expect that in drier weather, lower sump water volumes in shallower CBs would result in higher mean methoprene concentrations and a greater number of days with concentrations above the LC_{50}, and vice versa in wet weather due to dilution. However, evidence indicated the contrary. A hypothesis was drawn that methoprene in shallow CBs may be more susceptible to accelerated microbial and photolytic degradation in drier weather periods compared with the dilution and hydrolytic degradation in wet years. Greater sump water volume may protect and buffer methoprene from the former processes, which are also shown to occur at a lower rate than dilution and hydrolysis in a wet year. Further study of a longer time-series of in situ sump water levels

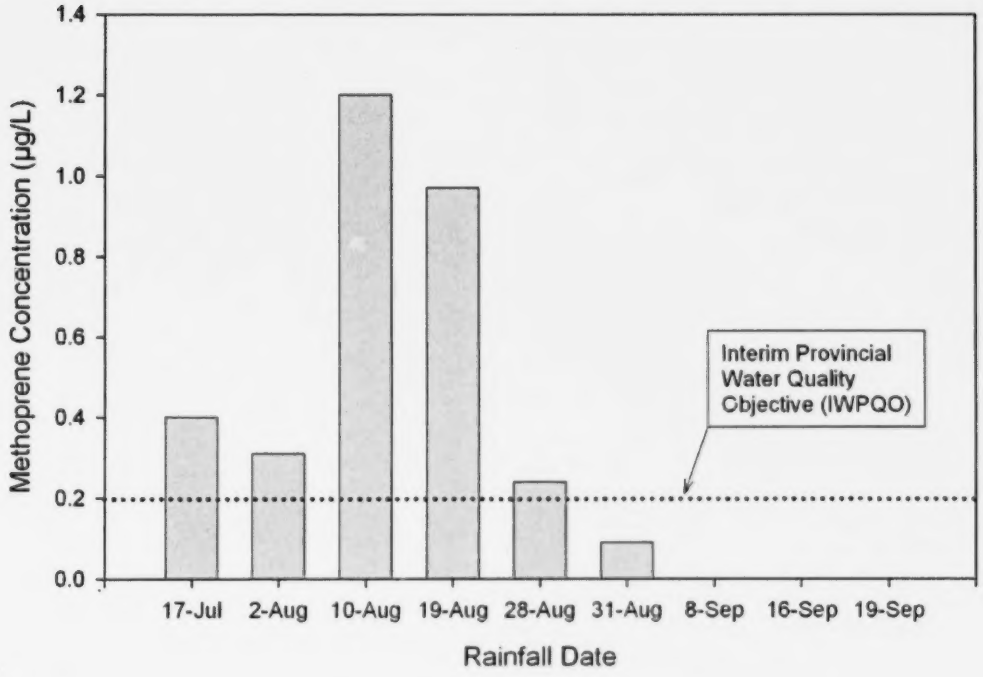

Fig. 7. Methoprene concentrations at the Newtonbrook sewer outfall over 2005 rainfall events.

and temperature, rainfall, and microbial and photolytic activity relative to methoprene concentrations within CBs and storm sewer outfall concentrations can better test this hypothesis.

In general, ingots were comparable in performance to pellets based on data in two similar wet years. Hence, and holding other cost factors equal, this research demonstrated that a single ingot dosage may represent a more cost-effective methoprene treatment regime than multiple pellet dosages. Further studies on the efficacy of methoprene in controlling larval emergence in these CBs are warranted notwithstanding the number of days above the LC_{50} concentration revealed in this research. As well the concurrent statistical analyses of methoprene metabolites in the daily methoprene samples, the interaction between methoprene and catch basin sediments, and other factors in the degradation of methoprene (such as temperature, light, and microbial activity), would be useful in fully understanding the advantages and disadvantages of the mosquito control program.

Acknowledgments

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Physicochemical Distribution of Metals in the Water Phase of Catch Basin Mixtures

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A mixture of sediment and water is formed during the cleansing of catch basins. This paper discusses the concentration levels and distribution of numerous metals and organic carbon (OC) in the water phase of this mixture. The results show that due to the high concentrations of metals in the water phase, the catch basin mixture should be treated before it reaches a recipient. Three sites with different types of area and traffic intensity were sampled. Four fractions were analyzed: unfiltered, dissolved (<0.2 µm), colloidal (0.22 µm to 1 kD [kilodalton]), and truly dissolved (<1 kD). The results of the unfiltered fraction show high concentrations of metals and OC in the catch basin mixture. A comparison of Canadian and Swedish Environmental Protection Agency guidelines and the catch basin mixtures shows that concentrations exceeded the threshold values for As, Cd, Cr, Cu, Ni, Pb, and Zn. Compared with samples from a reference lake in the area, the unfiltered fraction showed high concentrations of all elements. OC seems to have a large impact on the overall speciation of trace metals in the catch basin mixture. To trace the sources of the particulate fraction in the unfiltered samples, Al-normalization was used. Al-normalization indicated that Ca, K, Mg, Na, Mn, Ba, Co, and Cr concentrations could be explained by mineral particles used as traction control. Furthermore, the trace elements As, Cu, Pb, Zn, and Ni were all enriched in the catch basin mixture.

Key words: **stormwater, speciation, sources, ultrafiltration**

Introduction

The uptake of metals and other substances in flora and fauna is generally in a dissolved form (Sunda and Guillard 1976). Metals in natural water are distributed between three different fractions: particles, colloids, and a truly dissolved fraction. For example, Janssen et al. (2003) pointed out that the truly dissolved fraction and its speciation mainly determine bioavailability and thus the toxicity. Changes in environmental conditions (e.g., redox and pH) can strongly influence mobility and bioavailability by changing the speciation of metals (Ure and Davidson 2002). Hence, to understand stormwater and its effects on the environment, one must know the distribution of the elements in the water. The distribution is important not only for a biological (bioaccumulation, bioconcentration, bioavailability, and toxicity) understanding, but also for the geochemical (transport, adsorption, and precipitation) cycling of the elements (Florence et al. 1992). Metal distribution and bioavailable metals in stormwater have been investigated in very few studies, e.g., Wei and Morrison (1994), Brown (2002), and Björklund-Blom et al. (2002). A Canadian study where stormwater was collected from 14 different sources showed that stormwater could have toxic concentrations, depending on storm characteristics, season, source, timing during a storm, and overall drainage design (Marsalek et al. 1999). Kjølholt et al. (2001) showed that road runoff was toxic to algae. Lithner et al. (2003) showed that many trace elements in stormwater from Stockholm are directly bioavailable.

Stormwater quality is affected by rainfall, and in particular by the catchment where the major sources of pollutants are traffic (vehicles emissions, corrosion, and abrasion), road material, building material, animals, street litter, and spills (Butler and Davies 2000). Several studies over the last 30 years have shown stormwater to contain a wide range of polluting substances, such as organic substances, nutrients, trace metals, suspended material, and road salt (e.g., Sartor and Boyd 1972; Malmqvist 1983; Marsalek et al. 1997; Westerlund et al. 2003). Most of these pollutants are attached to different size particles (Stone and Marsalek 1996; Viklander 1998). Particles from roads and other sites are trapped in catch basins (gully pots) to protect the downstream sewer system or receiving waters as well as the sewer wall from sediment deposition. Biochemical reactions (e.g., anaerobic conditions) dominate in the catch basins during dry weather; physical processes dominate (e.g. resuspension of sediment) during wet weather (Butler et al. 1995; Morrison et al. 1995; Memon and Butler 2002a). According to Sartor and Boyd (1972), almost all particles greater than 246 µm are trapped in catch basins, whereas only 30% of the particles less than 43 µm are trapped. Grottker (1990) investigated catch basin sediment and showed that the highest concentrations of heavy metals were found in fractions less than 1.6 mm. However, according to Morrison et al. (1988) catch basins retain very little of the finest fractions, and Butler et al. (1995) stated that the metal concentration increases

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in the catch basin water between storm events due to the biochemical reactions during dry weather. Memon and Butler (2002b) concluded that catch basins are very ineffective in reducing dissolved pollutants.

When the grit chamber is full, the sediment and water are removed with the help of hydrodynamic pressure, and the standing water, sediment, and wash water are mixed together. The water phase of this mixture can be poured back into the catch basin, storm sewer, sanitary sewer, or surface water. This paper discusses the concentration levels and speciation of numerous metals and organic carbon (OC) in the water phase of this mixture (henceforth called catch basin mixture). Aluminum normalization was used to see if the metals could come from anthropogenic sources. This paper also investigates a wide range of metals to conduct a first screening of the content of metals in catch basin mixtures. Since this is just a first screening, no statistically based conclusions were drawn about the general distribution of metals in catch basins. However, this study could be of interest to owners/operators responsible for managing catch basins and government agencies responsible for protecting surface water quality to increase their knowledge of pollutants and their distribution within the water phase during the maintenance of catch basins.

Materials and Methods

Site Description and Sampling Procedure

The catch basin samples were taken during late autumn (November 2004) in Luleå, Sweden. Three sites with different traffic loads were chosen: catch basin 1, 500 vehicles per day; catch basin 2, 13,800; and catch basin 3, 25,500. The site with 500 vehicles per day is a housing area, while the other sites are in the city centre. The housing area consists of detached houses with private garages and is located in the outskirts of Luleå. Catch basin 2 is located next to a small green strip, and catch basin 3 is located next to a sidewalk. The cleaning frequency differs between the three catch basins. Catch basin 1 has not been cleaned for about the last 25 years, catch basin 2 is cleaned about every 10 years, and catch basin 3 is cleaned about every 5 years. Every year, approximately 6,000 to 7,000 tons of antiskid material (4 to 8 mm) is used in the city of Luleå, with approximately 50% of it removed in the spring through street sweeping. More anti-skid material is used in the city centre compared with the outskirts of the city. No de-icing salts are used in Luleå. The catch basin sediment and water were collected according to the general procedure in Sweden. The catch basins were emptied with a washed sludge vehicle, using hydrodynamic pressure and a vacuum to loosen and remove the sediment and water from the catch basin. The sludge vehicle had a capacity of 390 L/min at 13,000 kPa. The standing water, sediment, and wash water were mixed during transport in the sludge vehicle. When the mixture was discharged from the sludge vehicle, pH and oxygen were measured and water samples were collected for immediate analysis. These water samples represent water that could be poured back into the catch basin or surface water. The samples were collected in acid-washed plastic bottles and analyzed for suspended solids and metals. The metals were analyzed in four different fractions: unfiltered, dissolved (<0.2 μm), colloidal (<0.2 μm to 1 kD), and truly dissolved (<1 kD) fractions. The colloidal and truly dissolved fractions were obtained from ultrafiltration.

Ultrafiltration

The ultrafiltration technique used in this paper was cross flow filtration (Fig. 1). In a cross flow filtration process, the water sample is recirculated parallel to the filter membrane at a high flow rate, allowing particles and colloids to remain in suspension and prevent the filter from clogging. A hydrostatic pressure drives elements smaller than the pores of the membrane through the filter in the permeate container (truly dissolved fraction). Elements larger than the pores of the filter are concentrated in the retentate container (colloid fraction). Dahlqvist et al. (2004) further described the ultrafiltration technique.

The samples were prefiltered through a 0.2-μm filter before ultrafiltration. The colloidal fraction ranged from 0.2 μm to 1 kD, whereas the truly dissolved fraction is smaller than 1 kD (Fig. 2). During ultrafiltration, all samples were filtered through a 1-kD Prep-Scale-TFF-6 filter made of regenerated cellulose with a membrane area of 0.54 m^2. The pump used during ultrafiltration was a peristaltic base-plate pump. The retentate volume was kept constant at 2.5 L during the filtration process. The filter was rinsed with MilliQ water and solutions of NaOH (0.1 M) and HCl (0.5 M) after every filtration according to a procedure described by Ingri et al. (2000).

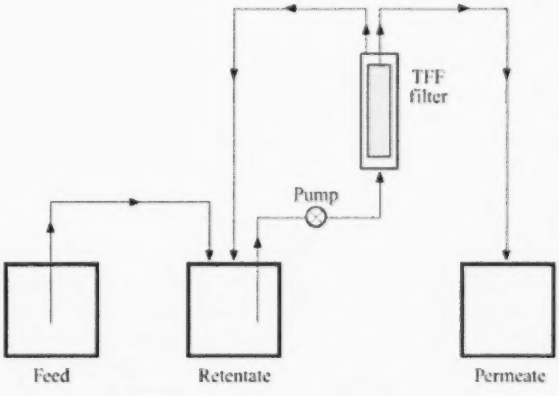

Fig. 1. Schematic set up of the ultrafiltration (TFF = tangential flow filtration) (Forsberg 2005).

The relationship between the permeate flow and the retentate flow is called cross flow ratio (CFR). For reliable results, Larsson et al. (2002) suggest a CFR above 15, though if the CFR is too low, elements can remain on the filter surface. The CFR is calculated according to equation 1:

$$CFR = \frac{F_{ret}}{F_{perm}} \quad (1)$$

where F_{perm} is the flow rate for the permeate ($L \cdot min^{-1}$) and F_{ret} is the flow rate for the retentate ($L \cdot min^{-1}$). The CFR was 200 for catch basins 1 and 2, and 40 for catch basin 3.

During ultrafiltration, the colloid fraction is enriched in the retentate, i.e., the retentate concentration has to be corrected to obtain the colloidal concentration in the original sample. This correction was done according to equations 2 and 3:

$$C_0 = \frac{C_{ret} - C_{perm}}{Cf} \quad (2)$$

$$Cf = \frac{V_{perm} + V_{ret}}{V_{ret}} \quad (3)$$

where C_0 is the original colloid concentration, C_{ret} is the measured colloid concentration, C_{perm} is the truly dissolved concentration, Cf is the concentration factor, V_{perm} is the permeate volume, and V_{ret} is the retentate volume.

Recovery

Calculating a recovery is common to verify if the different fractions are contaminated during ultrafiltration, or if parts of the fractions remain on the filter. Recovery (R) is calculated according to equation 4:

$$R = \frac{(C_{ret} + C_{perm})}{S} \quad (4)$$

where C_{ret} is the colloid concentration, C_{perm} is the truly dissolved concentration, and S is the initial concentration. If no elements are trapped in the filter, recovery (R) will be 1. The rinse solutions (NaOH and HCl) for the ultrafilter were analyzed. Adding these results to the mass in the permeate and retentate solutions allowed the calculation of a new adjusted recovery (R_a) according to equations 5 and 6:

$$C = \frac{(M_{ret} + M_{perm} + M_{NaOH} + M_{HCl})}{(V_{perm} + V_{ret})} \quad (5)$$

$$R_a = \frac{C}{S} \quad (6)$$

where C is the total mass of the elements per volume of water in the sample, M_{ret} is the mass of the elements in the retentate, M_{perm} is the mass of the elements in the permeate, M_{NaOH} is the mass of the elements in the NaOH solution, M_{HCl} is the mass of the elements in the HCl solution, and S is the initial concentration.

Laboratory Analyses

The samples were analyzed by Analytica AB. Analytica is accredited according to the international standard ISO 17025, ISO 9001:2000, SS EN 1484 and ISO/IEC Guide 25.

The standard method SS-EN 872:1996 was used for suspended solids; this standard is based on filtering through a glass-fibre filter with a pore size of 1.6 µm. To determine the concentration of suspended solids, the filters were weighed before filtration and then dried and weighed again after filtration. The lower limit of determination was 2 mg/L, without the establishment of

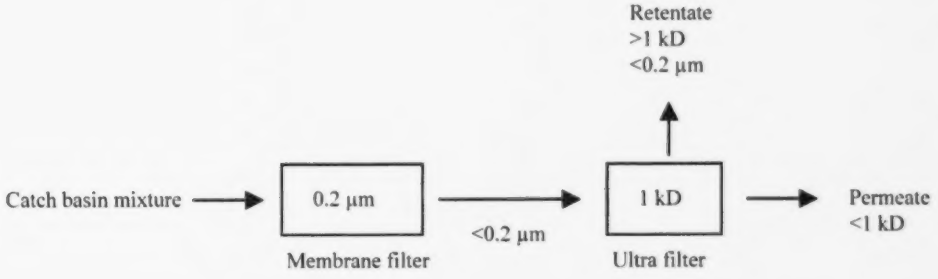

Fig. 2. Flow schema for the ultrafiltration procedure for the gully pot mixture.

an upper Limit (SIS 1996). The unfiltered phases were extracted before the analyses by digestion with a 20-ml sample and 2-ml suprapur HNO_3, which were processed in sealed Teflon containers in a specially modified microwave oven for 50 minutes at 160°C. The detection limits for the unfiltered samples were as follows: Ca (0.2 mg/L), Fe (0.02 mg/L), K (0.4 mg/L), Mg (0.14 mg/L), Na (0.5 mg/L), S (0.2 mg/L), Al (50 µg/L), As, Ba, and Cu (1 µg/L), Cd (0.05 µg/L), Co (0.2 µg/L), Cr and Mn (0.9 µg/L), Hg (0.02 µg/L), Ni and Pb (0.6 µg/L), and Zn (4 µg/L). The dissolved fractions were filtered through a 0.2-µm filter and before the analyses of the dissolved, colloid, and truly dissolved phase as well as the NaOH and HCl solutions, 1 ml of HNO_3 was added for every 100 ml of sample. The samples were analyzed through optical emission spectrometry with inductively coupled plasma (ICP-AES) and sector field mass spectrometry with inductively coupled plasma (ICP-SFMS). For mercury, atomic fluorescence spectrometry (AFS) was used in the analysis. Ca, Fe, K, Mg, Na, S, Al, Ba, Co, Cr, Cu, Mn, Ni, and Zn in the unfiltered samples and Ca, Fe, K, Mg, Na, S, Ba, Mn, Sr, and Zn in the dissolved, colloid, and truly dissolved samples were analyzed with ICP-AES. All remaining metals were analyzed with ICP-SFMS. Total organic carbon (TOC) was analyzed with the Shimadzu TOC-5000 high-temperature combustion instrument.

Results and Discussion

In all catch basins, the oxygen content (at slightly below 100%) and pH (7) were approximately the same.

The calculated recovery and the adjusted recovery for the catch basins are shown in Table 1. Considering the uncertainty of the ICP analysis, most of the recovery values are close to 1 (Fig. 3). Low recovery usually indicates that a fraction of the colloids was retained in the ultrafilter, a result that mainly influences the concentration in the retentate. As shown in Table 1, catch basin 2 has a lower recovery than the other catch basins, probably due to a lower cross flow rate at the end of the ultrafiltration, caused by problems with the pump. Recovery values become sensitive to small errors when metal concentrations are low. The higher recovery values for catch basin 3 indicate some type of contamination or problem with the analysis. However, these errors only affect the colloid concentration in catch basin 3 and do not influence the conclusions drawn in this paper.

The concentrations of suspended solids in the catch basin mixture increased with increasing traffic intensity (Table 2). The catch basins had high concentrations of suspended solids when compared with literature values for road runoff. According to, for example, Threllfall et al. (1991), Sansalone et al. (1998), and Westerlund et al. (2003), the concentration of suspended solids in road runoff is approximately 20 to 2,000 $mg \cdot L^{-1}$. However, the concentration of suspended solids in urban snow can be between 1,300 and 14,000 $mg \cdot L^{-1}$ (Viklander 1999; Reinosdotter and Viklander 2005), which corresponds well with the catch basin mixture, since both snow packs and catch basins accumulate large quantities of solids during an extended period.

TABLE 1. Recovery and mass balances for catch basin mixture 1, 2, and 3[a]

	Recovery			*Adjusted recovery*	
	CB 1 (500 v/d)	*CB 2 (13,800 v/d)*	*CB 3 (25,500 v/d)*	*CB 1 (500 v/d)*	*CB 3 (25,500 v/d)*
Ca	0.96	0.97	0.98	1.01	0.98
Fe	0.91	0.35[b]	1.41	0.93	1.57
K	0.99	0.94	1.01	1.05	1.01
Mg	0.96	0.98	0.98	1.01	0.98
Na	0.97	0.99	0.98	2.04	2.65
S	0.98	0.91	1.03	1.03	1.03
Al	0.88	0.48	1.43	0.91	1.56
As	0.89	0.15[b]	0.85	0.92	0.88
Ba	0.90	0.92	0.95	0.96	0.96
Cd	0.92	0.51	0.77	1.03	1.18
Co	0.73	0.31	0.46	0.83	0.60
Cr	0.93	0.43	1.37	0.97	2.00
Cu	0.67	0.46	1.05	0.76	1.23
Mn	0.94	0.90	0.95	1.01	0.96
Mo	0.96	0.89	1.03	1.01	1.03
Ni	0.75	0.39	0.46	0.88	0.79
P	0.90	0.93	1.73	0.95	1.81
Pb	0.84	0.28	1.44	0.87	1.80
Sr	0.96	0.96	0.98	1.02	0.99
Zn	0.65	0.31	0.39	0.76	0.57

[a] CB = catch basin; v/d = vehicles per day.
[b] Samples have no detectable truly dissolved fraction.

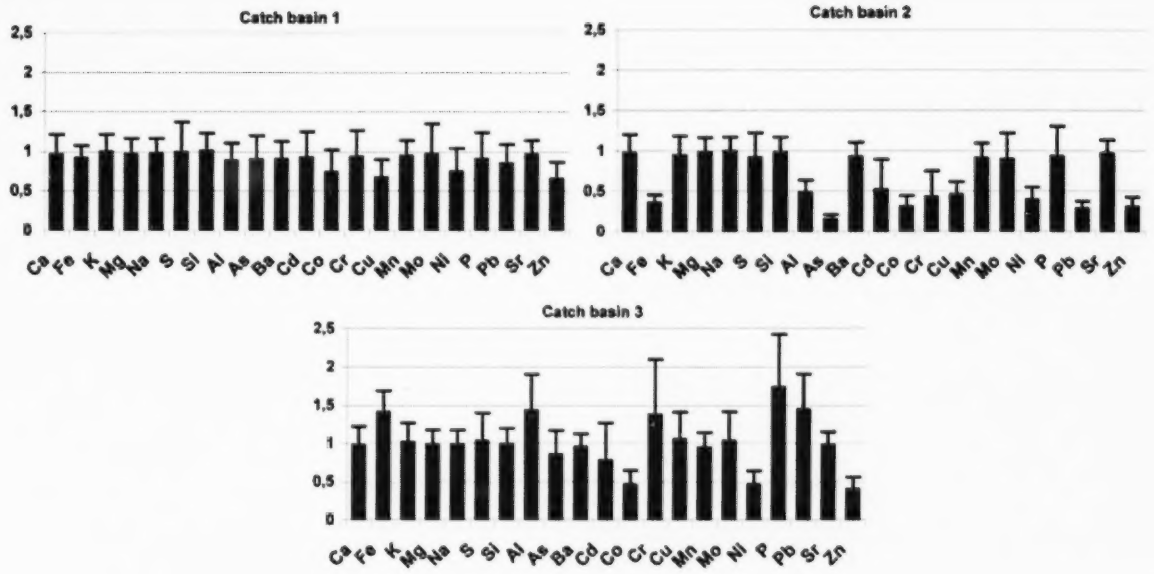

Fig. 3. Recovery values and the ICP-MS errors.

Overall, the catch basin mixture showed higher unfiltered concentrations of both major and trace elements compared with the reference lake water (Table 2). The TOC concentrations in the unfiltered fractions were substantially higher in the catch basin mixture and increased with increasing traffic intensity. Also, a large difference existed between concentrations in the unfiltered water (UF) compared with the dissolved (0.2-µm filtered) water in the catch basin mixture for all studied metals. Furthermore, catch basin 1 had relatively higher concentrations in the colloidal and truly dissolved fractions compared with catch basins 2 and 3. Comparing the reference lake's truly dissolved fraction with the catch basin mixture's truly dissolved fractions shows that the catch basins generally had higher values. Some elements differed less than others; Mg, S, Sr, and Pb had the smallest differences in concentration (less than four times), whereas Mn, Co, and Cd had substantially higher concentrations (more than 15 times) in the catch basin mixture compared with the reference lake.

The unfiltered Al concentration was highest in catch basin 3, but the highest dissolved (0.2-µm filtered) fraction was found in catch basin 1. Similarly, the dissolved (0.2-µm filtered) fractions for Fe, As, Cd, Co, Cr, Cu, P, Pb, Zn, and OC in catch basin 1 were much higher than in catch basins 2 and 3. For Al and Fe, more than 80% of their dissolved concentrations were in colloidal form, as opposed to Ca, K, Mg, and Na, which showed less than 10% (Ca has 15%) in the colloidal fraction. The high colloidal Al concentration in catch basin 1 was probably not caused by primary mechanically weathered minerals, i.e., detrital particles, since the total suspended solids were seven to eight times lower than in catch basins 2 and 3. Hence, the high colloidal fractions for Al (and to some extent Fe) and other trace metals were related to the high colloidal OC concentration in catch basin 1. The truly dissolved concentrations of Cd, Cr, Cu, and Zn in catch basin 1 were much higher than corresponding values in catch basins 2 and 3, possibly due to the relatively high truly dissolved fraction for OC in catch basin 1. This fraction was most likely an important complexing agent for the trace metals.

The large difference between unfiltered and dissolved (0.2-µm filtered) water in the catch basin mixture indicates that much of the high element concentrations in the unfiltered water was caused by suspended solids. For example, Ca data in catch basin 1 shows that approximately 90% of the Ca concentration in the unfiltered fraction was in a particulate form, whereas with the 0.2-µm filtered dissolved fraction, approximately 15% of the Ca was in colloidal form. Hence, to understand the composition of the unfiltered fraction, it is important to trace the origin of the particulate fraction. Al-normalization was used to trace the sources of the particulate fraction in the unfiltered samples. Aluminum is a major component in rock-forming minerals and its concentration in sediments and soils is usually a good indicator of detrital particles.

Table 3 clearly illustrates that the normalized concentrations of Ca, K, Mg, Na, Mn, Ba, Co, and Cr in the catch basin mixture were very similar to the local bedrock, Andesite. This similarity indicates that the high concentrations of these elements in the unfiltered samples were mainly caused by natural mineral particles used as traction control. Elements associated with the mineral fraction will also remain inert during sedimentation

TABLE 2. Concentrations for the catch basin mixtures and a reference lake for the different phases[a,b,c]

	Lake[d]				*Catch basin 1 (500 v/d)*				*Catch basin 2 (13,800 v/d)*				*Catch basin 3 (25,500 v/d)*			
	UF	*D*	*C*	*TD*	*UF*	*D*	*C*	*TD*	*UF*	*D*	*C*	*TD*	*UF*	*D*	*C*	*TD*
SS	–	–	–	–	2,300	–	–	–	4,100	–	–	–	17,800	–	–	–
Ca	2.7	2.6	0.7	1.7	135	15	2.0	12	133	19	0.2	18	233	22	0.6	21
Fe	0.9	0.5	0.3	0.005	336	5.3	4.7	0.1	226	0.06	0.02	<0.4	320	0.1	0.2	0.002
K	1.2	1.1	0.2	1.0	54	6	0.4	5.6	36	3.4	0.04	3.2	55	3.9	0.1	3.9
Mg	1.3	1.3	0.3	0.9	92	2.0	0.2	1.2	91	2.8	0.02	2.8	158	3.3	0.06	3.2
Na	3.3	3.3	0.3	3.0	94	60	3.5	55	49	25	0.2	24	80	34	0.6	33
S	2.8	2.7	0.5	2.2	22	3.2	0.8	2.4	11	2.8	0.2	2.4	16	2.6	0.4	2.2
Al	30	18	14	0.5	198×10^3	738	598	50	187×10^3	42	15	4	333×10^3	24	33	0.7
As	0.4	0.3	0.1	0.3	185	5.1	3.5	1.1	36	0.8	0.1	<0.005	48	3	0.2	2.4
Ba	4.9	3.3	1.4	8.1	2,280	38	11	23	2,280	48	0.5	44	3,600	73	2.2	67
Cd	0.003	0.002	0.002	<0.002	18	0.2	0.06	0.1	4	0.02	0.001	0.01	7.6	0.022	0.006	0.011
Co	0.2	0.06	0.06	0.008	145	1.2	0.4	0.5	170	0.5	0.02	0.1	247	2.3	0.07	1.0
Cr	0.2	0.2	0.09	0.03	705	4.0	3.4	0.3	364	0.2	0.06	0.02	527	0.1	0.1	0.03
Cu	0.8	1.3	0.5	0.4	1,800	22	12	3.2	1,060	3.1	0.7	0.7	1,880	2.3	1.7	0.7
Hg	<0.002	<0.002	<0.002	<0.002	1.6	0.003	<0.002	<0.002	0.5	0.003	5×10^{-4}	<0.002	0.34	0.003	0.003	<0.002
Mn	72	9.4	15	1.0	4,610	186	44	131	3,470	82	<0.03	75	4,640	365	6.2	339
Mo	0.2	0.2	0.02	0.2	n.a	10	2.0	8	n.a	2.4	0.2	2	n.a	12	1.3	11
Ni	0.7	0.7	0.3	0.3	392	5.5	1.7	2.5	270	1.0	0.06	0.3	412	3.9	0.3	1.5
P	20	13	10	1.1	n.a	78	59	11	n.a	16	5.6	9.8	n.a	12	19	2.3
Pb	0.2	0.14	0.1	0.01	5,080	70	59	0.02	571	0.7	0.2	0.01	588	0.3	0.4	0.01
Sr	22	21	5.9	15	n.a	47	6.1	39	n.a	31	0.3	30	n.a	58	1.6	55
Zn	1.4	1.9	0.7	0.3	7,150	82	36	17	4,240	5.8	0.7	1.1	5,820	14	1.9	3.9
TOC	12	9	7.1	3.7	300	58	17	38	580	3.2	0.85	2.3	1,200	12	5	8.8

[a] v/d = vehicles per day; UF = unfiltered phase; D = dissolved phase (<0.2 μm); C = colloid phase (<0.2 μm, >1kD); TD = truly dissolved (<1kD); SS = suspended solids.
[b] SS, Ca, Fe, K, Mg, Na, and S are in mg/L; the rest in μg/L.
[c] n.a. = not analyzed.
[d] Unpublished data.

TABLE 3. The ratio between the different elements unfiltered concentration and the aluminum unfiltered concentration[a]

	Andesite [b]	*Ryholite* [b]	*Soil* [c]	*SS* [d]	*SS, spring* [e]	*CB 1 (500 v/d)*	*CB 2 (13,800 v/d)*	*CB 3 (25,500 v/d)*
[f] Ca/Al	0.67	0.08	0.35	1.63	0.48	0.68	0.71	0.70
[f] Fe/Al	0.94	0.21	0.62	11.9	2.79	1.7	1.21	0.96
[f] K/Al	0.33	0.56	0.3	0.71	0.34	0.28	0.20	0.17
[f] Mg/Al	0.49	0.01	0.17	0.46	0.27	0.46	0.49	0.47
[f] Na/Al	0.22	0.35	0.39	0.57	0.27	0.47	0.26	0.24
[f] Al/Al	1	1	1	n.d.	n.d.	1	1	1
[g] As/Al	n.d.	n.d.	0.01	0.4	0.1	0.9	0.2	0.1
[g] Ba/Al	11.2	2.4	9.2	17	11	11.5	12.2	10.8
[g] Co/Al	0.5	n.d.	0.2	0.8	0.3	0.7	0.9	0.7
[g] Cr/Al	2.7	n.d.	1	2.8	1.4	3.6	2	1.6
[g] Cu/Al	0.9	n.d.	0.5	2.2	0.8	9.1	5.7	5.6
[g] Mn/Al	18.3	4.7	0	230	60	23.3	18.6	13.9
[g] Ni/Al	0.5	n.d.	0.3	0.9	0.5	2	1.4	1.2
[g] Pb/Al	n.d.	n.d.	0.1	0.9	0.3	25.7	3.1	1.8
[g] Zn/Al	1.7	0.3	0.6	n.d.	n.d.	36.1	22.7	17.5

[a] CB = catch basin; v/d = vehicles per day; n.d. = no data available.
[b] Andesite and Ryholite : bed rock in Luleå (Perdahl and Frietsch 1993).
[c] Soil samples are taken from the Kalix rivers catchment area.
[d] SS = Suspended solids, Kalix river.
[e] SS, spring = Suspended solids during spring, Kalix river.
[f] Units = $mg \cdot g^{-1}$.
[g] Units = $mg \cdot mg^{-1}$.

and early diagenesis in the sedimentary column. However, Cr is a common metal found in stormwater due to traffic being a major source (Muschak 1990); therefore, it could also be from anthropogenic sources. Iron increased slightly in catch basins 1 and 2, indicating some other phase besides detrital particles. However, this enrichment was much lower than that measured in many natural particles transported in the Kalix River (Table 3), indicating large enrichments because of secondary formed Fe-oxyhydroxides.

The trace elements As, Cu, Pb, Zn, and, to some extent, Ni were all enriched in the catch basin mixture. The ratio for As was not measured in the Andesite, though it was compared with the soil samples from the Kalix River (Table 3). As was elevated ten times or more in all three catch basin mixtures. Average suspend .d solids in the Kalix River generally showed a high enrichment of As due to the sorption of As onto the suspended Fe-oxyhydroxides. Fe was not greatly enriched in the catch basin mixtures; therefore, the enrichment of As could not be fully explained by the presence of Fe-oxyhydroxides. Cu, Pb, and Zn (and Hg and Cd, though they were not detected in the natural samples) showed a clear normalized enrichment in the unfiltered water from the catch basin mixture compared with all natural particles shown in Table 3. The enrichment of these elements in the unfiltered fractions could not be explained through detrital particles or Fe-oxyhydroxides. Table 2 clearly shows that much of the OC in the catch basin mixture was in particulate form. The enrichment of As, Cd, Cu, Hg, Pb, and Zn in the unfiltered fraction appears to be associated with the particulate organic fraction and/or sorbed onto the mineral particles, so it probably comes from anthropogenic sources. The sources of metals are many and depend on specific materials, land use, and local activities within the catchment areas. Possible sources within the catchment areas for the catch basins are traffic (e.g., tire wear, brake lining, motor oil, grease, and automobile exhaust), wear and leaching of the road, crash barriers, road signs, and atmospheric fallout.

The Swedish Environmental Protection Agency has conducted a quality criterion classification according to the concentration of certain metals in lakes and watercourses (SEPA 2001). The metals are classified into five different classes, with the possibilities for biological effects are found in classes 3 to 5 (Table 4). Biological effects can be found in waters in class 3, there is an increasing risk of biological effects in class 4, and a high risk for biological effects in class 5, even at a short exposure time. According to the Swedish Environmental Protection Agency, this guideline should be compared with the unfiltered concentrations. All compared metals had an unfiltered concentration that exceeded the threshold value for class 5 in one or more of the catch basins (Table 5). However, many of the dissolved metal concentrations also exceeded the guideline. The dissolved concentration of Pb in catch basin 1 was so high that it exceeded the threshold value for class 5, and the truly dissolved concentrations for Cd and Cu in catch basin 1 exceeded the threshold value for class 3. The concentrations in the catch basins were also compared with the Canadian water quality guidelines (Table 5), which have slightly lower threshold values than the Swedish guideline (Table 4). The unfiltered concentrations for all compared metals in all three catch basins exceeded the guideline, with some of the dissolved concentrations (As, Cd, Cu, Pb, and Zn) being over the threshold value, especially in catch basin 1. These guidelines are for the whole recipient, i.e., the catch basin mixture will be diluted. However, the toxicity is dependent on the sensitivity and

the water chemistry (e.g., the TOC concentration and its speciation) of the recipient, though long-term exposure of the polluted water will eventually affect the recipient (e.g., De Shamphelaere et al. 2003).

Conclusions

The catch basin mixture had higher unfiltered concentrations of both major and trace elements compared with the lake water. Furthermore, the high OC concentration observed in the catch basin mixture, compared with lake water, most likely had an impact on the speciation of trace metals in the particulate, colloidal, and truly dissolved phases in the catch basin mixture. OC probably worked as both a sorption phase and a complexing agent. The OC concentration appeared to be related to the number of passing vehicles.

The large difference between unfiltered and dissolved fractions (0.2-µm filtered) in the catch basin mixture shows that most elements were attached to particles. Catch basin 1 showed high truly dissolved concentrations for Cd, Cr, Cu, and Zn, which were probably related to the high concentration of truly dissolved OC. Aluminum normalization showed that the concentrations of Ca, K, Mg, Na, Mn, Ba, Co, and Cr could be explained by mineral particles, whereas the metals Cu, Pb, Zn, Ni, Cd, and Hg were enriched in the catch basin, so they probably came from anthropogenic sources.

However, with these high concentrations the catch basin mixture needs to be treated before it reaches a recipient. Therefore, more research regarding the distribution of metals in catch basins is needed.

TABLE 4. The Swedish Environmental Protection Agency guideline for metals in lakes and water courses, and the Canadian water quality guideline[a,b]

	Swedish EPA*			Canadian water quality guideline[c]
	Class 3	Class 4	Class 5	
As	5–15	15–75	>75	5.0
Cd	0.1–0.3	0.3–1.5	>1.5	0.017
Cr	5–15	15–75	>75	8.9[c]
Cu	3–9	9–45	>45	2–4
Hg	–	–	–	0.026
Ni	15–45	45–225	>225	25–150
Pb	1–3	3–15	>15	1–7
Zn	20–60	60–300	>300	30

[a] Sources: SEPA 2001; Environment Canada 2003.
[b] Units are all µg/L.
[c] Values are meant to protect all forms of aquatic life and all aspects of the aquatic life cycles, including the most sensitive life stage of the most sensitive species over the long term (Environment Canada 2003).
[d] Cr III.

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TABLE 5. The elements from the catch basins in different speciation compared with the SEPA classification and the Canadian water quality guideline[a,b,c]

	As	*Cd*	*Cr*	*Cu*	*Ni*	*Pb*	*Zn*
Swedish EPA[a]							
Class 3	1-D	1-D		1-TD			
		1-TD		2-D			
Class 4	2-UF			1-D			1-D
	3-UF						
Class 5	1-UF	1-UF	1-UF	1-UF	1-UF	1-UF	1-UF
		2-UF	2-UF	2-UF	2-UF	1-D	2-UF
		3-UF	3-UF	3-UF	3-UF	2-UF	3-UF
						3-UF	
Canadian water quality guideline[a]							
	1-UF	1-UF	1-UF	1-UF	1-UF	1-UF	1-UF
	1-D	1-D	2-UF	1-D	2-UF	1-D	1-D
	2-UF	1-C	3-UF	1-C	3-UF	1-C	1-C
	3-UF	1-TD		1-TD		2-UF	2-UF
		2-UF		2-UF		3-UF	3-UF
		2-D		2-D			
		3-UF		3-UF			
		3-D		3-D			

[a] Sources: SEPA 2001; Environment Canada 2003.
[b] 1 = catch basin 1 (500 v/d); 2 = catch basin 2 (13,800 v/d) and 3 = catch basin 3 (25,500 v/d); v/d = vehicles per day.
[c] UF = unfiltered phase ; D = dissolved phase; C = colloidal phase; TD = truly dissolved phase

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Reduction of Alkali-Labile Phosphates in Mussels Exposed to Primary-Treated Wastewaters Undergoing Ozone and Ultraviolet Disinfection: A Pilot Study

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The purpose of this study was to examine the estrogenic potential of a primary municipal effluent, undergoing ozone or ultraviolet disinfection, in *Elliptio complanata* mussels. Mussels were exposed for seven weeks, using a continuous flow-through system, to a primary effluent from a major city before and after disinfection. Results showed that the effluents, regardless of the disinfection procedure, readily affected gametogenesis in mussels as determined by gonado-somatic index, and by DNA synthesis as determined by the activity of aspartate transcarbamoylase activity, a rate-limiting enzyme for pyrimidine synthesis. The estrogenic potential of the effluents was observed by the increased levels of alkali-labile phosphate, a generic measure for vitellogenin-like proteins, where the disinfection procedures did not completely remove the estrogenic effects of the primary effluent. Thus, the introduction of an ozone or ultraviolet disinfection step to a primary-treated effluent will likely diminish the estrogenic potential, but not entirely.

***Key words*: mussels, municipal effluents, estrogenic potential, vitellogenin-like proteins, ozone, ultraviolet radiation, disinfection**

Introduction

The City of Montreal's (Quebec, Canada) wastewater treatment plant treats domestic and industrial wastewaters from a population basin of 1.7 million inhabitants. It uses enhanced physicochemical processes such as ferric and/or alum coagulation for removing suspended solids and phosphorus (Gehr et al. 2003). However, the microbial loading is still high (in the order of 1 million fecal coliforms per 100 mL) which compromises the quality of the receiving waters of the St. Lawrence River given the high flow rate of the effluent discharge (about 20 to 25 m^3/sec). In an attempt to reduce the bacterial loading of their effluents, various pilot-scale disinfection scenarios were examined, such as ozonation and photolysis by ultraviolet (UV) radiation. These treatments have proven effective in reaching the target level of 1,000 fecal coliform counts per 100 mL (Gehr et al. 2003). However, questions remained whether these treatments could modify the effluent matrix in such a way as to increase its toxicity.

Among the potential toxic effects observed in municipal wastewaters, their endocrine disruptive properties are noteworthy. The estrogenic chemicals (e.g., estradiol, ethynylestradiol, bisphenol A, and nonylphenol from the use of surfactants) found in these wastewaters are present at levels that induce the egg-yolk protein precursor vitellogenin (Vtg) and feminize feral fish (Diniz et al. 2005) and bivalves (Gagné et al. 2001; Blaise et al. 2003). Vtg's primary function serves as a source of energy for fertilized eggs, and hence the developing embryos.

The estrogenic and feminization potential of municipal effluents are well documented in fish (Diniz et al. 2005; Nakari 2004) and bivalves (Gagné et al. 2001; Blaise et al. 2003). Feminization of fish and mussels (sex reversal and intersex) could have profound impacts in the maintenance of populations (Grist et al. 2003). Since mussels are sedentary during their life-cycle, an increased female to male ratio can contribute to the local disappearance of mussel populations living near sources of municipal effluents.

Aspartate transcarbamoylase (ATC) is a rate-limiting enzyme for pyrimidine biosynthesis to support nucleic acid production in the developing gametes (Mathieu 1987). Its activity is enhanced during gametogenesis and closely follows the gonado-somatic index in bivalves. In female gonads, oocytes accumulate Vtg-like proteins as the main energy source for the developing embryo, which is partially under the control of estradiol-17β (Osada et al. 2003). Estrogens increase the levels of alkali-labile phosphate (ALP) which is considered to be an indirect assay of Vtg-like proteins in bivalves (Gagné et al. 2001, 2002). Moreover, exposure of bivalves to municipal effluents led to the induction of ALP in a dose-dependent manner in *Dreissena polymorpha* mussels (Quinn et al. 2004), *Elliptio complanata* mussels (Gagné et al. 2001), and *Mya arenaria* clams (Gagné et al. 2002), which makes these mussels useful models to monitor the estrogenic potential of complex mixtures to the benthic community.

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Ozone treatment holds promise in reducing the estrogenicity of complex wastewaters. Ozonation proved successful in removing 90% of spiked estradiol-17β and 17α-ethynylestradiol at a relatively low concentration of 1 µg/L (Hashimoto et al. 2006). However, effects on the "global" estrogenicity of municipal effluents were not tested and this question was investigated in the present study.

The purpose of this study was therefore to study the effects of either ozone or UV radiation disinfection on the estrogenic activity of the Montréal primary-treated municipal effluent, using the freshwater mussel, *Elliptio complanata*. Mussels were exposed for seven weeks in a continuous flow-through system to the primary effluent before and after UV or ozone treatments. Gonad integrity was examined by following changes in the gonado-somatic index, pyrimidine synthesis activity, and Vtg-like proteins in effluent-exposed mussels.

Methods

Elliptio complanata mussels were collected by hand in the Richelieu River. Mussels were transported at 4°C and placed in 300-L tanks filled with a continuous flow (circa 1 L/h) of UV-treated and charcoal-filtered tap water at 15°C. Mussels were allowed to acclimatize for one month and were fed twice a week with a commercial coral reef feed solution enriched with freshwater *Pseudokirchneriella subcapitata* algae (5 x 10^6 algae per tank).

Three types of effluent treatment were used in this experiment. First, the Montreal primary-treated effluent followed physical-chemical treatment (screening and suspended matter removal by the addition of ferric chloride or alum with the addition of FLO Polymer AE 440 surfactant) to partially remove solids and suspended materials. Second, the ozone treated primary effluent had been treated with ozone from a corona discharge ozone generator unit (Ozonia, Canada) delivering a maximal concentration of 9 mg/L of ozone in each of three columns (total ozone 27 mg/L of O_3, measured by means of a Mini-HiCon ozone analyzer). The system uses a 98% oxygen, 2% nitrogen delivery system, and has the capacity of treating 3,000 L/h of effluent. Third, the pilot-scale UV-treated primary effluent was developed by passing the primary effluent through a series of medium pressure mercury-based UV-emitting lamps at a wavelength of 254 nm and (Trojan 3000+ model) a mean dose of 31 ± 6 mJ/cm^2. No change in water temperature occurred because of the high flow rate of the effluent (circa 10 m^3/min). All three types of effluents stood for 2 h in holding tanks before exposing the freshwater mussels in the dark and without aeration. This simulates the time of release of the treated wastewaters from the plant to the point of discharge in the St. Lawrence River. Mussels were then exposed to 0, 1, 3, 10, and 20% vol/vol dilutions of the effluent for seven weeks at a temperature of 12 to 14°C in 60-L aquariums in continuous-flow mode with a flow rate of 1 L/h. The exposure tanks were aerated and mussels were fed on a weekly basis. Ten mussels were exposed to each effluent concentration for each effluent treatment group.

Estrogenic properties of the municipal effluents were examined by analysis of the gonado-somatic index, Vtg-like protein concentration, and gamete-associated DNA synthesis (ATC activity). The gonado-somatic index (GSI) was determined by weighing the freshly dissected gonad from the soft tissues mass (gram of gonad per gram of soft tissues). The gonad tissues were then homogenized with a Teflon pestle tissue grinder apparatus in 100-mM NaCl containing 10-mM Hepes-NaOH, pH 7.4, and 0.1 mM ethylenediamine tetraacetic acid (EDTA) and 0.1 mM dithiothreitol. The homogenate was then centrifuged at 15,000 x g for 30 minutes at 2°C and the supernatant was collected. The levels of Vtg-like proteins were determined in the supernatant by the ALP methodology (Gagné et al. 2001). The supernatant was mixed with acetone at 30% final concentration and centrifuged for 5 min at 10,000 x g. The pellet was resuspended in the homogenization buffer for gel electrophoresis analysis (Nupage precast 4 to 12% polyacrylamide high resolution gels, Invitrogen Inc., U.S.A.). The running buffer consisted of 50-mM MOPS (sodium 4-morpholinepropanesulfonate) buffer, pH 7.2, containing 1-mM EDTA and 0.2% sodium dodecylsulphate. For the ALP assay, a portion of the resuspended material was treated in alkali and the liberation of inorganic phosphates was determined as described. The data were expressed as micrograms of phosphate per milligr[illegible] of proteins. The biosynthesis of pyrimidine to sup[illegible] DNA synthesis for oocyte and spermatozoid produc[illegible]n was followed by the rate-limiting enzyme ATC activity in the gonad (Mathieu 1987) using a special extraction procedure for the simultaneous estimation of orthophosphate and carbamoylphosphate (Herries 1967). The data were expressed as the rate of phosphate formation (µg) normalized with time and total protein content.

Ten mussels were exposed to each effluent concentration and the exposure experiments were repeated three times. Critical differences between control and treated cells were determined by an analysis of variance followed by Dunnett's *t* test. A correlation analysis was performed with the Pearson-moment method. The threshold concentrations were obtained by the geometric mean of the lowest effect concentration, and the no effect concentration in percent vol/vol: (lowest effect concentration x no effect concentration)$^{1/2}$. Significance was set at $p < 0.05$.

Results and Discussion

The primary effluent was treated to either UV radiation or ozone for disinfection purposes. The primary effluent usually contained between 20 to 50 mg/L of suspended solids, but had relatively high concentrations of fecal coliforms in the order of 1 million total coliforms per

100 mL (Purenne 2006). Ozone disinfection had no significant effects on residual ammonia, the nitrite to nitrate ratio, or total and dissolved organic carbon content (Gagné et al. 2007a). The ozone treatment led to increased saturation in oxygen (90%) with an increase in the redox potential starting at -250 millivolts up to 550 millivolts, with a mean ozone concentration of 16.5 mg/L before the 2-h preincubation step. Both treatments were able to reduce the levels of fecal coliform, enterococci bacteria, and coliphages (Hébert et al. 2008). In this study, fecal coliforms dropped from 400,000 counts per 100 mL in the primary-treated effluent to 10,000 and 50,000 bacteria counts per millilitre with UV and ozone disinfection strategies, respectively. However, ozone disinfection was much more effective than UV in reducing coliphage counts: from 800,000 counts per 100 mL in the primary-treated effluent to 260,000 and circa 1,000 counts for the UV and ozone disinfections, respectively. These results support the notion that the performance of disinfection strategies should not be based on only one target organism, but on other species such as parasites, viruses, and other bacteria (Gehr et al. 2003). Mussel mortality events (18%) were observed at the highest concentration of the primary-, ultraviolet-, and ozone-treated effluents at the end of the exposure period. This indicates that both disinfection strategies did not introduce acutely lethal toxicity into the primary-treated wastewater.

After exposure for seven weeks to the effluents, the gonad size was significantly affected by all three types of effluents (Fig. 1). In the primary- and the ozone-treated effluents, the GSI was somewhat reduced but the reduction was not significant with respect to the unexposed group. In the UV-treated effluents, the GSI dropped 1.2-fold at a threshold concentration of 14% vol/vol, corresponding to 0.3 to 1 km downstream of the dispersal plume in the river. The decrease was also significantly different from the primary-treated effluent at the same concentration. This suggests that the disinfection strategy could mitigate the inhibitory effects of the effluent towards the relative gonad size in freshwater mussels. Reduced GSI was also found in carps exposed in a flow-through system to 100% vol/vol of a treated domestic effluent (Diniz et al. 2007). ATC activity was readily reduced for all three effluent treatments (Fig. 2). At effluent concentrations greater than 3%, the ozone treatment reduced the ATC activity more than the UV treatment and the primary effluent, suggesting that ozone treatment can worsen the responses. Freshwater mussels exposed to aeration lagoons also displayed reduced ATC activity with a concomitant elevation of ALP in gonad tissues (Gagné et al. 2007b). Gel electrophoresis of the gonad supernatant extracts revealed two female-specific high molecular weight protein bands corresponding to >250 and 200 kDa respectively (Fig. 3). These bands were not detected in males nor in sexually undifferentiated mussels. The molecular weights of Vtg are in the same range as those found in *Elliptio complanata* mussels (Won et al. 2005). Moreover, ALP levels were significantly correlated with the protein band density at 250 to 275 kDa (r = 0.7; p = 0.02). This supports the contention that ALP was associated with Vtg-like proteins as determined by gel electrophoresis analysis in this study.

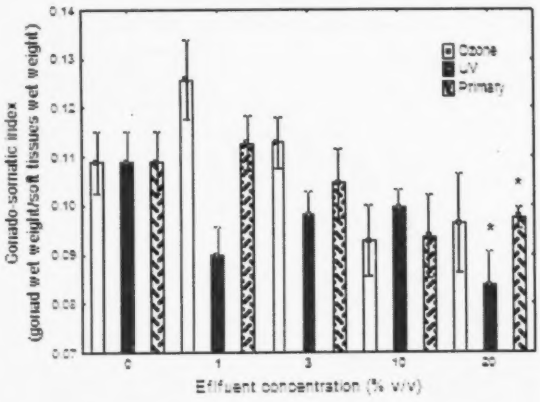

Fig. 1. Changes in the gonado-somatic index in freshwater mussels exposed to treated effluents at varying concentrations. Mussels were exposed for seven weeks to the primary effluent and primary effluent with ozone or UV treatment and the gonado-somatic index was determined. The data represent the mean with the standard error. The stars * indicate significant differences compared with controls (0% vol/vol).

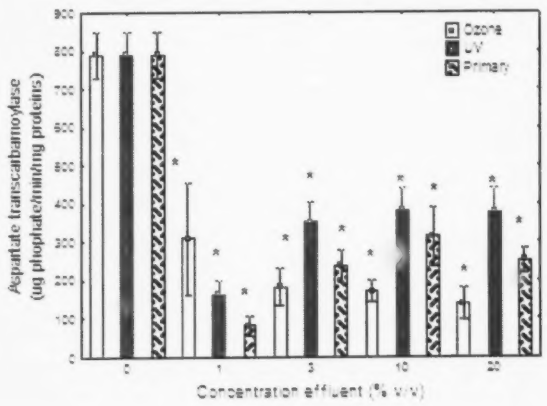

Fig. 2. Changes in gametogenic activity in mussels exposed to the treated effluents at varying concentrations. Mussels were exposed for seven weeks to the primary treated effluent and primary treated effluent with ozone or UV treatment, and gametogenic activity was determined by ATC activity. The data represent the mean with the standard error. The stars * indicate significant differences compared with controls (0% vol/vol).

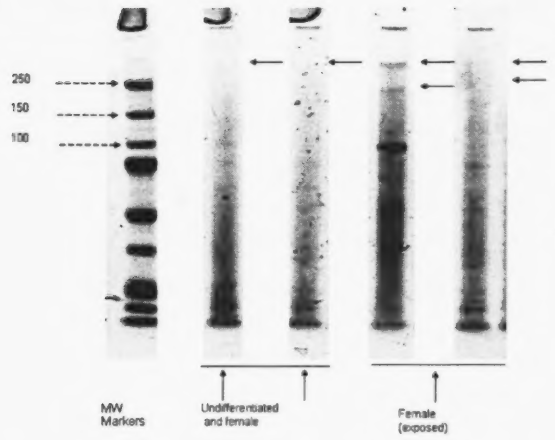

Fig. 3. Protein gel electrophoresis analysis of gonad tissue extracts. The acetone-fractionated gonad homogenate were resolved by gel electrophoresis. The gels revealed two female-specific high molecular weight protein bands at >250 and 200 kDa.

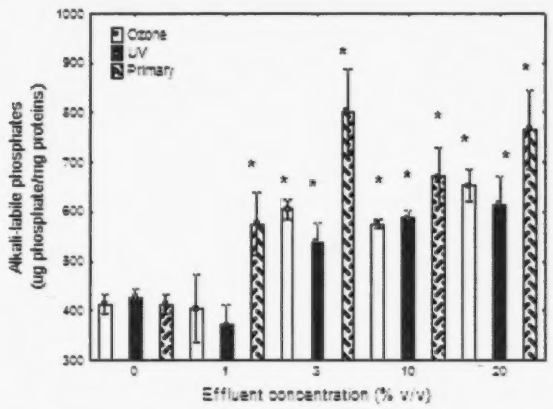

Fig. 4. Changes in ALPs in mussels exposed to the treated effluents at varying concentrations. Mussels were exposed for seven weeks to the primary-treated effluent before and after either ozone or UV treatments, and Vtg-like proteins were determined by ALP measurement from gonadal tissue. The data represent the mean with the standard error. The stars * indicate significant differences compared with controls (0% vol/vol).

Exposure to the municipal effluents significantly increased the levels of ALP in the mussels (Fig. 4). For the primary effluent, ALP levels increased 2.1-fold with respect to the controls at a threshold concentration of 1.7% vol/vol. In the UV-treated effluent, the ALP levels increased 1.4-fold at a threshold concentration of 1.7% vol/vol. This increase was however significantly lower than the ALP levels in mussels exposed to the primary-treated effluent. For the ozone-treated effluent, the ALP levels rose 1.5-fold at a threshold concentration of 1.7% vol/vol. As with the UV-treated effluent, the increase in ALP levels was significantly lower than those obtained from the primary-treated effluent. The data suggest that the estrogenic potential of the effluents was somewhat reduced by either UV or ozone disinfection treatments, but these treatments were not enough to completely remove the estrogenic effects. Ozone treatment of municipal effluents was shown to alleviate in vitro estrogenic effects of other effluents, although some compounds still persisted after ozonation (Snyder et al. 2006). In another study, ozonation of a municipal effluent removed up to 90% of added estradiol-17β, estrone, and 17-α ethynylestradiol at an ozone dose of 1 mg/L, and these levels dropped to below detection limits with ozone at concentrations >3 mg/L (Hashimoto et al. 2006). An estrogenic potential was detected in zebra mussels exposed to a tertiary-treated effluent in Ireland after 112 days of exposure to the effluent (Quinn et al. 2004), suggesting that the estrogenic potential of urban effluents are persistent and resilient to various disinfection treatments.

Although ozone and UV could significantly reduce the levels of estrogens in water, the reduction was apparently not enough to completely eliminate the estrogenic effects in mussels exposed continuously for seven weeks to these effluents. Based on the threshold concentrations of the observed effects and the dilution rate of the effluent plume, the effects would be observed at a distance of 8 km for the primary-treated, UV-treated, and ozonated effluents. These results corroborated the observed estrogenic and feminization effects in caged mussels in the dispersion plume of the same primary-treated effluent at a distance of 8 km for one year (Blaise et al. 2003).

Conclusions

The ozone and UV treatment of a physical- and chemical-treated effluent reduced the estrogenic potential in comparison with the primary-treated effluent. However, neither UV nor ozone disinfection scenarios were able to completely remove the estrogenic effects of the effluent to the freshwater mussel.

Acknowledgments

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Estimation of Biodegradation and Liquid-Solid Partitioning Coefficients for Selected PAHs in Municipal Wastewater Treatment

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Batch testing was employed to estimate model parameters that are required for predicting the fate of polynuclear aromatic hydrocarbons (PAHs) in wastewater treatment. Linear partitioning was found to describe the partitioning of PAHs to solids and was best described when the soluble phase of the PAHs was determined by centrifugation alone. The liquid-solid partitioning coefficients obtained for primary and secondary sludges were statistically different, with the latter being higher than the former for most of the PAHs examined in this study. Temperature had a significant impact on the estimated biodegradation rate coefficients (K_b). The biodegradation rate coefficients for anthracene and phenanthrene (three-ring PAHs) were statistically different from benzo(a)anthracene and chrysene (four-ring PAHs). The presence of a nitro-adduct on acenaphthene resulted in a substantial increase in the K_b relative to the unsubstituted anthracene and phenanthrene. A sensitivity analysis revealed that the removal of PAHs in a full-scale wastewater treatment plant was most sensitive to the value of the liquid-solid partitioning coefficients. Approximately 60% of the PAHs were removed from the wastewater stream through partitioning to both primary and secondary solids, and subsequent discharge.

Key words: **model, fate, biodegradation, polynuclear aromatic hydrocarbons, liquid-solid partitioning**

Introduction

Despite efforts to control their release into sewer systems, polynuclear aromatic hydrocarbons (PAHs) are consistently observed in municipal wastewaters (Bergqvist et al. 2006; Busetti et al. 2006; Vogelsang et al. 2006). Often the concentrations of these substances in wastewaters are below the traditional analytical method detection limits, although they are regularly detected in the sludge streams due to increased solids concentrations (Harrison et al. 2006; Kinney et al. 2006).

PAHs are of concern because of their potential toxicity during chronic exposures and because of their potential to bioaccumulate. The Canada-Ontario Agreement on the Great Lakes has identified 17 PAHs as Tier-2 contaminants and requires the development of policies and practices that restrict their release into the Great Lakes (EC and MOE 2007). The United States Environmental Protection Agency has designated PAHs as Priority Pollutants, and these form part of the list of 126 regulated chemical pollutants (U.S. EPA 1974).

The development of policies related to controlling discharges of these substances into the aquatic environment and into biosolid streams can be better informed by improved estimates of their fate and removal in wastewater treatment processes. However, the difficulties associated with measuring these substances in wastewater streams presents significant challenges related to quantifying their removal in wastewater treatment processes. Hence, modelling of the fate of these substances in wastewater treatment can be useful in evaluating treatment performance when developing policy options.

Partitioning to suspended solids and biodegradation are the mechanisms which are anticipated to have the greatest impact upon the fate of multi-ring PAH's in wastewater treatment processes. The relatively low Henry's law coefficients and the strong partitioning of PAHs with three and four rings to solids indicates that volatilization of these PAHs will be minimal (Manoli and Samara 2008). There are however relatively few reports in the literature that document measured values of liquid-solid partitioning and biodegradation rate coefficients in wastewater treatment systems. Dobbs et al. (1989) developed a correlation between liquid-solid partitioning coefficients and the octanol-water partitioning coefficients of a cross section of compounds. However, in their study, PAHs were not included in the compounds that were employed to develop the correlations. Subsequent studies (Melcer et al. 1995; Manoli and Samara 2008) have applied this correlation to PAHs, but there has been no direct experimental verification.

The availability of biodegradation rate coefficients for PAHs in municipal wastewater treatment is also very limited. Coburn et al. (1988) estimated biodegradation rate coefficients for a limited number of low molecular weight PAHs, mostly naphthalene and methyl-naphthalenes, from a sampling and analytical study of industrial wastewater impoundments. At the same time, Coburn et

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al. (1988) also estimated biodegradation rate coefficients for higher molecular weight PAHs from data published in the technical literature. Manoli and Samara (2008) observed discrepancies between the removals predicted by the U.S. EPA FATE model and those calculated using data obtained from a full-scale wastewater treatment plant, suggesting that the parameters employed in this model require calibration.

The objectives of this study were to develop measured values for the liquid-solid partitioning and biodegradation rate coefficients for selected complex PAHs in municipal wastewater treatment. The coefficients were determined by conducting bench-scale testing with sludges and wastewaters obtained from a full-scale wastewater treatment plant. The impact of temperature on the rate of biodegradation and the effect of partitioning of PAHs to colloidal solids were also investigated in the experimental plan. Liquid-solid partitioning coefficients were determined for primary and secondary (waste activated) sludges separately. Preliminary modelling that was conducted using estimates of biodegradation and liquid-solid partitioning coefficients from the literature (Coburn et al. 1988; Dobbs et al. 1989) indicated that volatilization of the target compounds in the experimental systems would be minimal and hence measurements of volatilization were not included in the experimental plan. The coefficients that were estimated from the bench-scale testing were then implemented into the TOXCHEM+ fate model (Hydromantis Inc., Hamilton, Ontario). The model was then applied to the full scale wastewater treatment plant that was the source of the sludge samples for lab testing for sensitivity analysis purposes.

Approach

The target substances that were evaluated in this study reflected a range in the number of aromatic rings as well as the number of substitutions with nitro groups, and included anthracene, phenanthrene, benzo(a)anthracene, chrysene, 2,4-dinitrotoluene, and 5-nitroacenaphthene. The partitioning and biodegradation of these compounds was investigated in the wastewater and sludge streams that were generated by a full-scale wastewater treatment plant that is located in southern Ontario. The full-scale facility employs conventional primary settling, activated sludge with a solids residence time of 5 to 12 days as secondary treatment, and sand filtration as a tertiary treatment for enhanced solids removal.

Partitioning Tests

The liquid-solid partitioning tests involved dosing inactivated sludge samples with a mixture of the target compounds, contacting the liquid and solid phases for 4 hours, and then measuring the concentrations of the target compounds in the total sample as well as two different soluble phases. A 4-hour period has been demonstrated to be adequate for establishing equilibrium with respect to sorption in previous studies of adsorption of organics onto wastewater treatment solids (Dobbs et al. 1989). Sorption to primary sludge (PS) and sorption to waste activated sludge (WAS) were characterized separately. The loading of the target compounds to the sludge solids was varied by conducting a series of tests in which the dosing level of the target compounds in the samples was maintained constant while the concentrations of solids in the samples were varied.

At the end of the liquid-solid contacting period, the soluble concentrations were determined by two sample-processing methods in order to facilitate an assessment of the impact of colloidal-scale particles (particles approximately <0.45 µm) on the soluble phase concentrations. In one of the sample processing methods, the decant that was obtained after centrifugation alone was employed for contaminant characterization. These samples would be expected to contain some level of colloidal-scale solids that would maintain some of the target compounds in solution. The second processing method involved initial flocculation with 50 mg/L of alum prior to centrifugation. The decant that was obtained from the combined flocculation-centrifugation was characterized for organic contaminant concentrations. These samples would be expected to have reduced concentrations of colloidal matter due to the flocculation step.

Replicate tests were completed for the PS and WAS, and hence a total of four test events were completed in this project. For each test, approximately 80 L of each type of sludge was obtained from the full-scale wastewater treatment plant. Each sludge volume was initially concentrated by settling and decanting the supernatant. The concentrate was subsequently diluted with the decant to generate four samples, each with a volume of 12.0 L, but with differing concentrations of suspended solids. The samples had target volatile suspended solid (VSS) concentrations of either 0.1, 0.5, 1.0, or 2.0 g of VSS per litre. The samples were then halved to generate subsamples of 6.0 L each. Each of the subsamples was dosed to obtain a 0.1% concentration of sodium azide in solution to inhibit microbial activity during the test. The subsamples were contacted with the sodium azide for a period of 14 hours to allow for biomass inhibition. Each of the subsamples was then dosed with a suite of concentrated solutions that contained the target contaminants to obtain a target concentration of 500 µg/L of each substance in the sample. The subsamples were mixed by magnetic stirrers in 12 glass jars for a period of 4 hours at a temperature of 22°C.

At the end of the contacting period, a 1.0-L sample of each solution was collected and preserved with concentrated H_2SO_4 to a pH less than 3.0 prior to submission to the laboratory for analysis. The remaining volume was then further divided into equal volumes of 0.5 L each. Sample 1 was centrifuged immediately at a rotational velocity of 3,000 rpm for a period of 10 minutes. After centrifugation, the decant was poured into sample bottles, preserved as described previously,

and then submitted for analysis. Sample 2 was dosed with 50 mg/L of alum and then gently stirred at 30 rpm for a period of 15 minutes to facilitate flocculation. After the flocculation step was completed, sample 2 was centrifuged and decanted in a manner that was identical to that employed for sample 1.

Biodegradation Tests

Biodegradation testing was performed in batch tests with a duration of 5 days. Two batch reactors that were mechanically stirred and had a liquid volume of 37.0 L were employed to provide replicate data. The reactors were of glass construction, and all materials contacting the reactor contents were either glass or stainless steel. At the beginning of the batch tests, a mixture of primary clarifier effluent and aeration basin mixed liquor from the full-scale wastewater treatment plant was added to the batch reactors. Warm condition tests were conducted at room temperature (20 to 22°C) while cold testing was conducted in a cold room at a temperature of 4°C.

VSS concentrations in the batch reactors were measured and were in the range of 1,400 to 1,900 mg/L. Mixing was initiated and the reactors were dosed with stock solutions containing the target compounds. Individual stock solutions were prepared and consisted of the target compound dissolved in a solution consisting of deionized water and ethanol/methanol. A volume of each stock solution was added to the batch reactors with the objective of achieving a target concentration of 100 µg/L of each analyte in the reactor at the beginning of the test.

The reactors' contents were sampled for the target compounds immediately prior to dosing in order to quantify any background concentrations. Samples of the reactor contents were collected immediately after dosing and subsequently at times of 8 hours, and 1, 2, 3, 4, and 5 days after dosing in the warm temperature tests, and at times of 2, 4, and 8 hours and then 1, 2, 3, 4, and 5 days after dosing in the cold temperature tests. The collected samples were acidified to a pH of 3 and then stored in a refrigerator at 4°C prior to submission to the laboratory for analysis.

Analysis of PAHs consisted of in situ acetylation and liquid-liquid extraction with dichloromethane. The extracts were then dried using sodium sulphate and concentrated prior to instrumental analysis. The analysis was performed using a gas chromatograph-mass spectrometer (GC-MS) operated in the selected ion monitoring (SIM) mode.

Several statistical tests were employed in the course of this work. Standard linear regression was employed to estimate the slope (K_p) and y-intercepts (b), along with the standard errors of these values for the linear partitioning equation. The coefficients were subsequently tested to determine if they were statistically different from zero using *t*-tests (Zar 1984). Separate liquid-solid partitioning coefficients (K_p) were estimated for each compound for each sludge type tested. For each compound, the K_p values were compared between sludge types using *t*-tests. Standard linear regression was employed to estimate the first-order decay coefficients (k') and the standard errors associated with these values. A *t*-test (Zar 1984) was then employed to determine whether the values of the decay coefficients were statistically different from zero.

Results and Discussion

Partitioning Tests

Liquid-solid partitioning coefficients were determined for those target compounds which demonstrated a statistically significant trend between liquid and solid phase concentrations. Duplicate partitioning tests were conducted for each sludge type, and the results of both tests were combined to facilitate estimation of the partitioning coefficients that best fit the overall data set. A linear partitioning model was employed as per equation 1 and was fit by linear regression:

$$\frac{X}{M} = K_p C_s + b \qquad (1)$$

where X = mass of compound associated with the solids (µg);
M = mass of volatile suspended solids (g VSS);
K_p = liquid-solid partitioning coefficient (L/g VSS);
C_s = soluble concentration of compound (µg/L); and
b = y intercept (µg/g).

Two types of soluble samples were analyzed in this study to obtain insight into the effect of colloidal solids on the estimation of liquid-solid partitioning coefficients. Samples that would have some amount of colloidal solids present were prepared by centrifuging samples and decanting the liquid component into the sample bottles. For the purposes of this discussion, these samples will subsequently be referred to as centrifuged. Samples that would have less colloidal solids present were generated by dosing the samples with alum, allowing them to flocculate, and then centrifuging the samples and subsequently decanting the liquid phase into sample bottles. This procedure is commonly employed to determine the true soluble chemical oxygen demand that is present in wastewater samples when characterizing them for modelling purposes (Mamais et al. 1993). For the purposes of this discussion, these samples will subsequently be referred to as flocculated.

Figures 1 and 2 present the best fit sorption isotherms for chrysene in the PS sludge samples, while Fig. 3 and 4 present the values for the WAS samples. The responses observed in these figures are typical of those observed with the other target compounds. From these figures it can be observed that, with some experimental scatter, the linear isotherms reasonably described the liquid-solid partitioning behaviour. The use of linear isotherms was deemed to be appropriate on the basis of the generally

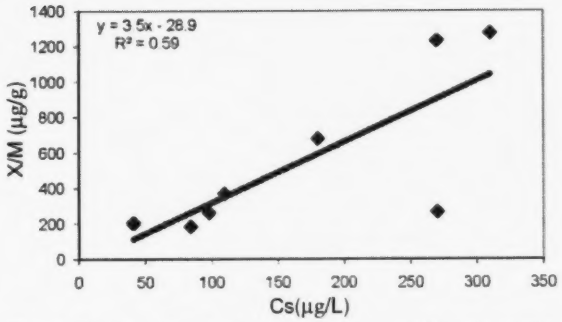

Fig. 1. Partitioning of chrysene to PS—centrifuged samples (*X/M* = solid phase concentration).

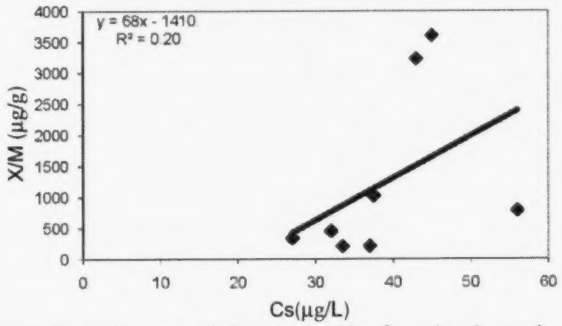

Fig. 2. Partitioning of chrysene to PS—flocculated samples (*X/M* = solid phase concentration).

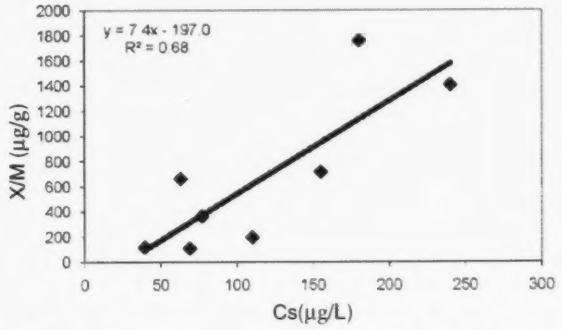

Fig. 3. Partitioning of chrysene to WAS—centrifuged samples (*X/M* = solid phase concentration).

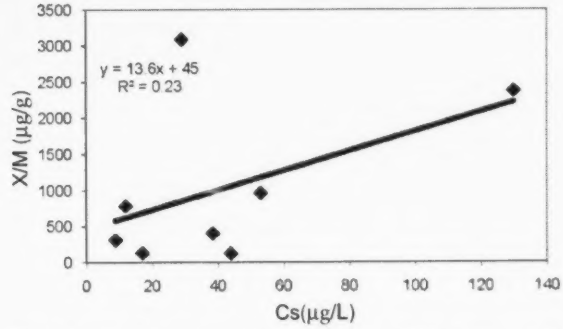

Fig. 4. Partitioning of chrysene to WAS—flocculated samples (*X/M* = solid phase concentration).

random distribution of residuals about the best fit line when all tests were considered collectively. The data generated in the centrifuged samples were more linear in nature than the flocculated samples, and there was less scatter of the data about the best fit line for the former samples.

The estimated liquid-solid partitioning coefficients are summarized in Tables 1 and 2 for PS and WAS, respectively. The liquid-solid partitioning relationships that were formulated on the basis of the centrifuged soluble samples had y-intercepts that were relatively small and not statistically different from zero. The slopes of these lines were statistically significant at a 95% level of significance. Those that were generated on the basis of the flocculated samples had relatively large y-intercept values, and in most cases there was substantial uncertainty in these values as indicated by the large standard errors of the estimated values. The slopes of these lines were not statistically significant at a 95% level of significance. The partitioning of contaminants to wastewater solids has traditionally been described by first-order partitioning relationships where the y-intercept values would be equal to zero (Dobbs et al. 1989). The results obtained for the centrifuged samples would appear to concur with previous trends, while the results obtained with the flocculated samples deviate from previous trends.

The slopes of the partitioning relationships (as indicated by the K_p values) were substantially greater for the flocculated dataset as compared with the centrifuged data set. In some cases, the flocculated K_p values were more than 10 times the values that were based upon the centrifuged samples. The increases in K_p values for the flocculated samples were much greater than could be explained by the reductions in the soluble concentrations alone, and hence would suggest that the solid-phase concentrations (*X/M*) may have been somewhat in error.

The underlying cause of the liquid-solid partitioning patterns that were observed with the flocculated samples (i.e., negative y-intercepts and exceptionally high K_p values) is not readily apparent. The results suggest that there may have been an additional variable that was affecting the results and that this variable was changing when the solid-phase concentrations were varied. Hence, the slopes of the isotherms were exaggerated and the y-intercepts were depressed. It is likely that the addition of alum to the bottles resulted in a change to the properties of the solids in the test bottles. The charge distribution on the aluminum hydroxide flocs would be expected to be substantially different than for the sludge particles, resulting in different sorption properties for the various organics. Since solids concentrations in the bottles were varied in order to change the liquid-solid ratios, it may be that there was an interaction between the solids concentrations and the alum that was effectively greater at the lower solids concentrations which corresponded to the higher soluble phase concentrations. Given the uncertainties associated with this phenomenon, subsequent application of the K_p values only employed those obtained with the centrifuged samples.

TABLE 1. Summary of primary sludge sorption partitioning coefficients[a]

Substance	Centrifuged					Flocculated				
	K_p (L/g)		b (µg/g)		r^2	K_p (L/g)		b (µg/g)		r^2
	Est.	Std. Err.	Est.	Std. Err.		Est.	Std. Err.	Est.	Std. Err.	
Anthracene	5	0.88	-26.8	158	0.84	36.9	24.9	-1062	1641	0.27
Phenanthrene	5	0.86	-70.4	143	0.85	19.1	2.43	-652	229	0.92
Benzo(a)anthracene	7.9	1.7	-111	216	0.78	128.9	44.5	-3104	1503	0.58
Chrysene	3.5	1.2	-28.9	228	0.59	68	56	-1411	2226	0.2
5-Nitroacenapthene	1.9	0.65	-83	195	0.59	3.3	0.54	-249	144	0.87

[a] K_p = liquid-solid partitioning coefficient ; b = y intercept; Est. = estimate; Std. Err. = standard error.

TABLE 2. Summary of waste activated sludge sorption partitioning coefficients[a]

Substance	Centrifuged					Flocculated				
	K_p (L/g)		b (µg/g)		r^2	K_p (L/g)		b (µg/g)		r^2
	Est.	Std. Err.	Est.	Std. Err.		Est.	Std. Err.	Est.	Std. Err.	
Anthracene	8.3	1.26	-109	142	0.9	36	7.37	-770	394	0.8
Phenanthrene	7.3	1	-155	128	0.9	15	1.43	-351	132	1
Benzo(a)anthracene	14	0.74	-40	37	1	39	4.65	-34	109	0.9
Chrysene	7.4	2.05	-197	274	0.7	14	10.2	456	565	0.2
5-Nitroacenapthene	0.6	0.86	212	228	0.1	0.3	0.58	191	165	0.1

[a] K_p = liquid-solid partitioning coefficient; b = y intercept; Est. = estimate; Std. Err. = standard error.

It was expected that the removal of colloidal solids during flocculation would have resulted in lower values of the soluble concentrations, and this was consistently observed. Hence this would support the hypothesis that colloidal solids increase the concentrations of "effectively soluble" contaminants in wastewater samples. Hence, colloidal matter would increase the transport of substances through physical treatment processes such as clarifiers. Future model enhancements should consider the role of colloidal solids in the transport of hydrophobic substances in wastewater treatment plants. Improved techniques for characterizing the partitioning of compounds to wastewater colloids would be required to facilitate this enhancement of the model.

The modelling of liquid-solid partitioning in wastewater treatment plants has typically assumed equivalent partitioning coefficients of organic compounds to primary and secondary solids (Dobbs et al. 1989). The results obtained in this study allowed for a comparison of the partitioning coefficients that were generated with differing solids types. The coefficients were compared using a *t*-test, and for the five substances that were common to the different sludges, all of the K_p values were found to be statistically different. The K_p values for anthracene, phenanthrene, benzo(a)anthracene, and chrysene in the WAS samples were approximately twice those that were observed in the PS samples. All of these substances are relatively hydrophobic and had the highest K_p values observed in this study. The K_p value for 5-nitroacenapthene, which is a less hydrophobic compound, was higher for the PS test as compared with the WAS test. For the purposes of the subsequently described modelling of the biodegradation test data, the K_p values obtained with the WAS samples were used.

Biodegradation Tests

Figure 5 presents the concentrations of chrysene that were measured in the batch biodegradation reactors operating under warm and cold conditions. The trends observed for chrysene are typical of those observed for the other target compounds. From Fig. 5, it can be seen that under the warm test conditions, the concentrations of chrysene declined as the biodegradation test progressed. It can also be observed that the results of the duplicate tests were consistent with each other, thereby implying good reproducibility of results.

The responses observed under the cold temperature conditions were considerably different from the warm test conditions. From Fig. 5, it can be seen that at cold temperatures the chrysene concentrations varied somewhat randomly with no consistent trend in concentration with time. The differing behaviours observed at the two temperatures clearly demonstrate the impact of temperature on the removal of PAHs. The substantially lower removals at the cooler temperature strongly suggests that biodegradation was responsible for the observed total PAH removals.

The batch testing that was conducted in this study measured the total concentration of the contaminants in the samples versus time. Modelling the biodegradation of trace contaminants has typically been assumed to follow first-order kinetics with respect to soluble substrate concentrations (Rittmann and McCarty 2001). Hence,

regression was employed to estimate an overall first-order decay coefficient (k') for each compound in each batch test under both warm and cold temperature conditions, where:

$$\frac{dC}{dt} = k'C \quad (2)$$

The value of k' describes the overall decline in contaminant concentration in a sample, and incorporates the biomass concentration as well as the effect of partitioning of the contaminant to solids. Figure 6 presents the results of the model fitting for chrysene for the warm temperature conditions as an example and is typical of that observed for the other target compounds under the same conditions. From Fig. 6 it can be observed that the first-order model was able to effectively describe the change in contaminant concentrations with time.

A mixed first-order model was subsequently employed in this study to describe the rate of biodegradation of the target compounds, as per equation 3:

$$r_b = k_b X C_s \quad (3)$$

where: r_b = rate of biodegradation (µg/L-d);
k_b = biodegradation rate coefficient (L/g of VSS-d);
X = biomass concentration expressed as VSS (g of VSS/L);
C_s = soluble concentration of contaminant (µg/L).

The relationship between k_b and k' is described in equation 4:

$$k_b = \frac{k'(1+K_p X)}{X} \quad (4)$$

where: K_p = liquid-solid partitioning coefficient for WAS (L/g of VSS); X = biomass concentration measured in batch tests (as VSS), (g of VSS/L).

The k_b values were estimated from the k' values that were determined for each batch test. The average value for each temperature condition was calculated from the replicate batch tests. The estimated k_b values along with their standard errors are summarized in Table 3. The standard errors associated with the k_b values incorporated the standard errors associated with the k' coefficients as well as the K_p coefficients. In the warm temperature tests, the concentrations of 5-nitroacenapthene and 2,4-dinitrotoluene declined so rapidly that k_b values could not be estimated. In the cold temperature tests, the decline of the PAHs was so little that, when the variability in the data was considered, the decay coefficients were not statistically different from zero.

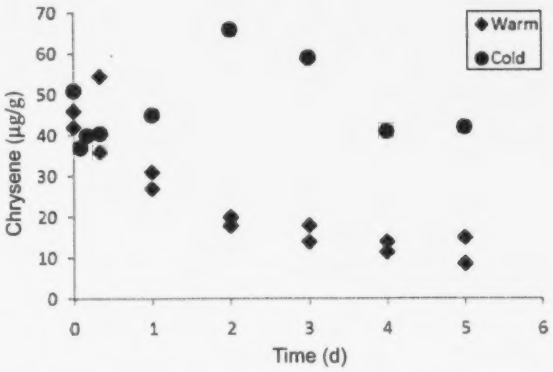

Fig. 5. Chrysene concentrations in biodegradation tests.

From Table 3 it can be seen that the k_b values generally decreased as the complexity and size of the substances increased. Anthracene and phenanthrene are both three-ring compounds, and there was no statistical difference between the rate coefficients determined for the warm test condition. Benzo(a)anthracene and chrysene are both four-ring compounds, and had k_b values that were similar in magnitude but statistically different from the three-ring compounds. 5-Nitroacenaphthene is also a three-membered ring compound; the presence of the nitro-adduct appeared to have resulted in a substantial increase in the k_b in the warm test condition relative to the unsubstituted anthracene and phenanthrene. It is also clear that temperature had a substantial impact on the rate of biodegradation. However, it was not possible to estimate temperature adjustment coefficients since k_b values for the same substances were not available for both temperatures.

A sensitivity analysis was conducted to assess the impact of uncertainty in the K_p and k_b values on the predicted fate of the compounds. The sensitivity analysis

TABLE 3. Summary of estimated biodegradation rate coefficients k_b(L/g-d)[a]

Substance	*Molecular weight*	*Warm tests*		*Cold tests*	
		Est.	*Std. Err.*	*Est.*	*Std. Err.*
Anthracene	178	9.3	2	NA	NA
Phenanthrene	178	8.5	2.2	NA	NA
Benzo(a)anthracene	228	3.6	0.6	NA	NA
Chrysene	228	2.5	0.8	NA	NA
5-Nitroacenapthene	199.2	ND	ND	2.2	0.11
2,4-Dintrotoluene	182.1	ND	ND	0.6	0.06

[a] Est. = estimate; Std. Err. = standard error; NA = not statistically different from zero; ND = not available due to rapid degradation.

was conducted using the configuration and operating data that were available for the wastewater treatment plant that was the source of the sludges employed in the batch testing. The sensitivity analysis varied one parameter at a time, and the fate with regards to the extent of biodegradation and partitioning to the sludge streams and the final effluent were estimated. Each parameter was varied over a range that spanned from 50 to 200% of the value that was estimated in the batch testing program.

As an example, Fig. 7 summarizes the fate of chrysene as a function of the K_p value and is typical of the other PAHs that were characterized in this study. From the curves, it can be seen that the fraction of the chrysene that was predicted to be present in the final effluent of the plant was relatively insensitive to the K_p values. A three-fold increase in K_p resulted in a reduction of the effluent fraction by only 10%. In part this could be attributed to the presence of sand filters that were employed at the wastewater treatment plant to remove a majority of the suspended solids from the wastewater. The fraction of the compounds that was biodegraded was also relatively insensitive to K_p. This response decreased by about 15% when the K_p value was varied by three-fold. The compounds that were assessed in the sensitivity analysis are all relatively hydrophobic with elevated K_p values. Hence, even relatively large uncertainty in K_p values would not be expected to have much impact on the availability of these compounds for biodegradation. The prediction of the fraction of the compounds that would be present in the sludge streams was most sensitive to variations in K_p. Over the range of K_p values that were evaluated in this study, the fraction predicted to be present in the sludge streams varied by approximately 20 to 30%. Given the hydrophobicity of the compounds, the high dependence of this response on K_p values would be expected.

Figure 8 presents the sensitivity of the model predictions for chrysene to the value of k_b. From these curves it can be seen that the model predictions were relatively insensitive to k_b over the ranges evaluated. The fraction that was predicted to be biodegraded increased by approximately 10% over this range, while the decreases in the predictions of compounds that were present in the final effluent and sludge streams were correspondingly less than 10%. The relative insensitivity to k_b was likely primarily due to the relatively high K_p values for the target compounds that therefore tended to favour their removal with waste solids as compared with biodegradation when these two removal mechanisms functioned competitively in a continuous flow system.

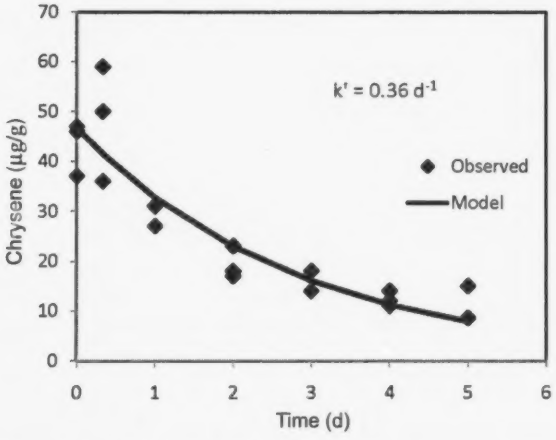

Fig. 6. Fit of first-order decay model: chrysene, warm temperature.

Conclusions

Biodegradation rate coefficients and liquid-solid partitioning coefficients were determined for a selection of polynuclear aromatic hydrocarbons. Linear partitioning described the partitioning of the PAHs to solids, but liquid-solid partitioning was better described when the soluble phase of the PAHs was determined by centrifugation relative to preliminary flocculation followed by centrifugation. The results from the flocculation approach suggested that there was an interaction between the solids and the flocculant that impacted on the liquid-solid partitioning. While the solids-flocculent interaction made it difficult to apply the results of these tests directly, it would appear that colloidal solids can increase the apparently soluble concentration of hydrophobic PAHs. This may increase the mobility of these compounds in wastewater treatment plants and their treated effluents, and should be studied in more detail. The potential effect of the contaminant-

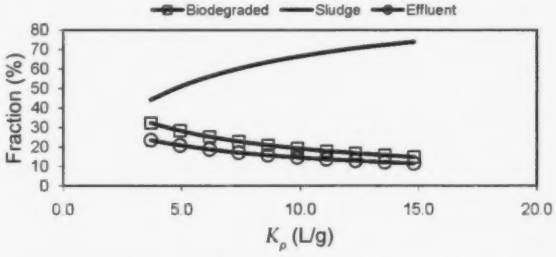

Fig. 7. Sensitivity of chrysene fate to K_p.

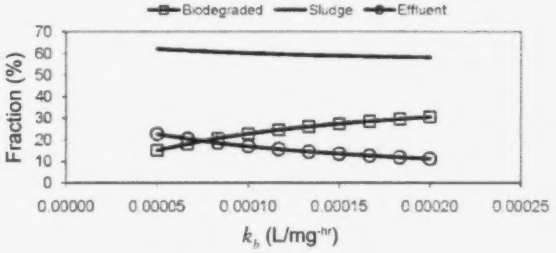

Fig. 8. Sensitivity of chrysene fate to k_b.

bearing colloids in municipal effluents to organisms in the aquatic environment also warrants investigation. The liquid-solid partitioning coefficients obtained for primary and secondary sludges were statistically different with the latter being higher than the former for most of the PAHs examined in this study. This observation differs from that which is employed in most common models of contaminant fate in wastewater treatment.

Biodegradation rate coefficients (k_b) were determined under warm and cold temperature conditions. Biodegradation was found to be first-order with respect to the soluble concentrations of the PAHs. Temperature had a significant impact on the estimated biodegradation rate coefficients. Anthracene and phenanthrene are both three-membered ring compounds and there was no statistical difference between the rate coefficients determined for the warm test conditions. Benzo(a)anthracene and chrysene are both four-membered ring compounds, and had k_b values that were similar in magnitude and statistically less than the three-ring compounds. The presence of a nitro-adduct on acenaphthene resulted in a substantial increase in k_b in the warm test condition relative to the unsubstituted anthracene and phenanthrene.

A sensitivity analysis revealed that the removal of PAHs in a full-scale wastewater treatment plant was most sensitive to the value of the liquid-solid partitioning coefficients. Approximately 60% of the PAHs were removed from the wastewater stream through partitioning to solids and subsequent discharge in the sludge streams.

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Heavy Metals Removal by Hydroxide Precipitation and Coagulation-Flocculation Methods from Aqueous Solutions

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The hydroxide precipitation and coagulation-flocculation methods were used to treat wastewater containing lead, zinc, copper, and iron. The concentrations of heavy metals in the synthetic wastewater range from 1 to 14 mg/L for lead, 5 to 90 mg/L for zinc, 3 to 90 mg/L for copper and 5 to 45 mg/L for iron. Individual Zn(II) and Cu(II) with concentrations below 90 mg/L and Fe(III) with concentrations below 45 mg/L were removed up to 99% by the precipitation method in the pH range of 8.7 to 9.6, 8.1 to 11.1, and 6.2 to 7.1, respectively. Though the highest percent removal of Pb(II) by hydroxide precipitation alone was approximately 98%, the final dissolved concentrations did not fulfill the Standard A discharge limit required by the regulations, thus further treatment by the coagulation-flocculation process was performed. Aluminum sulphate (alum), polyaluminum chloride (PACl) and magnesium chloride ($MgCl_2$) have been used as coagulants together with Koaret PA 3230 as coagulant aid to determine the effectiveness of the coagulation method for the removal of individual heavy metals in the wastewater. The effects of parameters such as pH, type, and dosage of coagulant on the percentage of metal removal, and the amount of coagulant aid on the flocs settling time were investigated. The jar test showed that up to 99% removal of Pb(II) was attained by the addition of 1,200 mg/L of alum, 150 mg/L of PACl, and 2,000 mg/L of $MgCl_2$ in a pH range of 6.5 to 7.8, 8.1 to 8.9, and 9.7 to 10.9, respectively.

Key words: **precipitation; coagulation-flocculation, heavy metals**

Introduction

Heavy metal pollution is an existing and growing worldwide problem, especially in developing countries. Heavy metals such as Pb, Zn, Cu, and Fe are often discharged by metal plating, metal cleaning and fabrication, battery manufacturing, chemical manufacturing, and paint and pigment industries. The treatment and removal of heavy metals have drawn considerable attention because of their association with various health problems. Although metals such as Mn, Fe, Cu, and Zn are essential nutrients at low levels (but are toxic at higher concentrations), others such as Hg, Cd, and Pb could bring severe physiological or neurological consequences even in small amounts (Angino et al. 1977; Maessen et al. 1985; Laws 1993; Nebel and Wright 1996; Macchi et al. 1996; Mohammed and Najar 1997).

Owing to the harmful effects of heavy metals to human beings and to aquatic life, permissible limits have been set by environmental authorities for different kinds of waters. In Malaysia, industrial wastewater discharge is regulated by *Sewage and Industrial Effluent Regulations*, 1979 (EQA 1974 [2002]). Various waste constituents may have to be removed or reduced to meet standard discharge limits before being released to the receiving streams. Currently, most of the industries in Malaysia treat their wastewater in order to meet the Standard B discharge limits. The Standard B discharge limits for lead, zinc, copper, and iron are 0.5 mg/L, 2.0 mg/L, 1.0 mg/L, and 5.0 mg/L, respectively. However, the Department of Environment of Malaysia may raise the industrial discharge limits to become more stringent, especially in the heavy metal concentrations, for protection of the environment from serious pollution in the future. Considerable investment and research have been focused on the improvement of many well-established technologies. Common technologies for the removal of heavy metals from aqueous solutions include chemical precipitation, coagulation-flocculation, ion exchange, and adsorption (Clifford et al. 1986; Grasso et al. 1990; Chung 1997; Mellah and Chegrouche 1997; Mohammed and Najar 1997; Eckenfelder 2000).

The heavy metal concentrations after a precipitation process alone do not necessarily accomplish the limit of pollutants required by the regulations, which is one of the most important criteria in choosing a treatment process (Netzer et al. 1974; Baltpurvins et al. 1995). Even though heavy metal concentrations in the final effluent may meet the discharge limit, the precipitates are too small and take a long time to settle. This is not desirable since a long settling time requires a larger settling tank. Normally, the processes that form the basis for the treatment of heavy metals begin with hydroxide precipitation, followed by coagulation-flocculation-settling, and subsequently the separation of the unsettled flocs from the wastewater stream by filtration.

Coagulation-flocculation is a commonly used physico-chemical method in the treatment of metal-bearing industrial wastewater because it removes

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colloidal particles, some soluble compounds, and very fine solid suspensions initially present in the wastewater by destabilization and formation of flocs (Burke et al. 2000). Both aluminum and ferric salts, either in monomer or polymeric forms, have been reported as effective coagulants in treating heavy metals from wastewater (Hannah et al. 1977; Chu 1999; Fan et al. 2003; Kang et al. 2003). Magnesium chloride, as compared with aluminum or iron salts, is a less commonly used coagulant in the field of wastewater treatment. It has been used in a study to investigate the effectiveness of the coagulation process for the removal of colouring matters (Tan et al. 2000; Ooi et al. 2005; Wong et al. 2007). It has been shown that the presence of Mg enhanced the removal of some pollutants (Leentvaar and Rebhun 1982). The effectiveness of seawater liquid bittern as a source of Mg to remove heavy metals has been evaluated (Ayoub et al. 2001); it gave a removal of 92.2, 75.2, and 63.2% for Pb(II), Zn(II), and Cu(II), respectively, at a pH range of 11.0 to 11.5.

It is important to investigate and determine the effectiveness of hydroxide precipitation and coagulation-flocculation in removing heavy metals (lead, zinc, copper, and iron) without major modification of the current wastewater treatment facilities in order to meet the Standard A discharge limits of 0.1 mg/L for lead, 2.0 mg/L for zinc, 0.2 mg/L for copper, and 1.0 mg/L for iron. The effects of parameters such as pH, type, and dosage of coagulant on the percentage of metal removal and the amount of coagulant aid on the flocs settling time have been studied.

Materials and Methods

The experiments conducted were part of the study of a Master's Degree which had been carried out in the Environmental Laboratory, School of Industrial Technology, University Science Malaysia. All experiments were conducted under the room temperature.

Chemicals

Lead(II) nitrate, zinc(II) sulfate heptahydrate, copper(II) chloride dihydrate (Merck KGaA, Germany) of purity >99%, and iron(III) nitrate nanohydrate (Fluka Chemie, Switzerland) of purity >97% were used to prepare the individual heavy metals solutions. Sodium hydroxide, NaOH of purity 99% supplied by Merck KGaA, Germany, was used as the base. Alum of industrial grade and PACl (30%) in powder of analytical grade were obtained from T.C. Chem. Technology (Kulim, Kedah, Malaysia), while magnesium chloride of analytical grade was supplied by Fluka Biochemika. Polyelectrolyte, Koaret PA3230 of commercial grade from Giulini Chemie was used as the coagulant aid throughout the experiment at a concentration of 0.1 g/L. All heavy metal solutions, coagulants, coagulant aids, and sodium hydroxide were prepared by using distilled water.

Analyses

The pH of the solution was measured by using a HACH Sension 3 pH meter (HACH, Colorado, U.S.A.), while the concentrations of the heavy metals were determined using a Perkin-Elmer A. Analyst 100 Atomic Absorption Spectrophotometer (Perkin Elmer, Singapore).

Jar Tests

The experimental work was divided into two parts. The first part consisted of experiments to determine and compare single metal removal by means of hydroxide precipitation. The percent of metal removal with respect to increasing initial concentrations was studied at various pH levels. Different amounts of NaOH were added to adjust the pH of 150-mL heavy metal solution. The solution was stirred for 1 minute by using the jar test apparatus, and allowed to settle for 30 minutes. The content was then filtered by using Whatman No. 4 filter paper. The pH and the metal concentrations of the supernatant were measured.

In the second part, a coagulation-flocculation process was carried out on Pb at a concentration of 7 mg/L since this is the highest concentration normally found in battery manufacturing wastewater. All experimental work was conducted by using a six-beaker jar test apparatus. Each beaker contained 150 mL of the heavy metal solution. The pH of the solution was adjusted by adding NaOH prior to the addition of coagulant. The samples were mixed at 60 to 65 rpm for 3 minutes. Coagulant aid was then added and the samples were allowed to mix further for 1 minute, followed by 30 minutes of settling. At the end of the settling period, the samples were filtered and analyzed for the concentration of the heavy metal ions. The conditions of the experiments are summarized in Table 1.

Results and Discussion

The Effect of pH on Metal Hydroxide Precipitation

The results of hydroxide precipitation on the selected heavy metal ions are illustrated in Fig. 1 to 4, where the percent removals of Pb(II), Zn(II), Cu(II), and Fe(III), respectively, are plotted against solution pH. Pb(II), Zn(II), Cu(II) and Fe(III) were found to form precipitates at various pHs in the absence of coagulants. All metals precipitate as hydroxides by the addition of NaOH. For each metal concentration, a curve with a maximum point, which represents the highest percentage of metal removal (minimum solubility), was obtained. These maximum points fell in a pH range of 7.8 to 8.8, 8.7 to 9.6, 8.1 to 11.1, and 6.2 to 7.1 for Pb(II), Zn(II), Cu(II), and Fe(III), respectively. The results agree with those reported in the literature (Hautala et al. 1977; Eckenfelder 2000; Kim et al. 2002).

The percent removals of Pb(II) were 69.0, 93.3, 96.9, and 98.3% for the initial concentrations of 1.5, 3, 7, and

TABLE 1. Summary of the conditions of experiments

(a) Hydroxide precipitation

Type of metal	*Concentration range (mg/L)*	*pH range*
Pb(II)	1–14	4–11
Zn(II)	5–90	3–11
Cu(II)	3–90	4–11
Fe(III)	5–45	2–11

(b) Coagulation-flocculation process on Pb(II) of 7mg/L

Type of coagulant	*Coagulant dosage (mg/L)*	*pH range*	*0.1 g/L coagulant aid (mL)*
Alum	200–4,000	4–11	2
PACl	150–1,200	4–10	2
$MgCl_2$	600–6,000	9–12	2

14 mg/L, respectively. The results show that the removal efficiency increased with the initial metal concentration. Though the highest percent removal of Pb(II) was approximately 98%, the final dissolved concentrations (i.e., 0.235 mg/L) do not fulfill the discharge limit required by the regulations, thus further treatment by the coagulation-flocculation process was performed.

Figure 2 shows a plot of percent removal of Zn(II) at different pH values. A similar plot is that of Pb(II) (Fig. 1), with a maximum point corresponding to the minimum solubility of Zn(II) and that falls in the pH range of 8.7 to 9.6 for each Zn(II) concentration; the results obtained are in agreement with those reported in the literature (Baltpurvins et al. 1996; Saari et al. 1998). According to Baltpurvins et al. (1996), the minimum Zn(II) solubility point falls in the pH range of 9.5 to 10, whereas Saari et al. (1998) indicated that the respective pH range was slightly lower (8.5 to 9.5). The percent removal of 10 mg/L of Zn(II) found in this study was 99.7%, which is higher compared with the 97.3% reported by Saari et al. (1998). Both minimum solubility points fall in the same pH range. The percent removal of Zn(II) increased tremendously from pH 5 to 7. An average increment of 53.6% removal was observed in that pH range for 5, 8, and 10 mg/L of Zn(II). Between a pH of 7 to 9.6, the final concentrations of Zn(II) (at <0.406 mg/L) in the

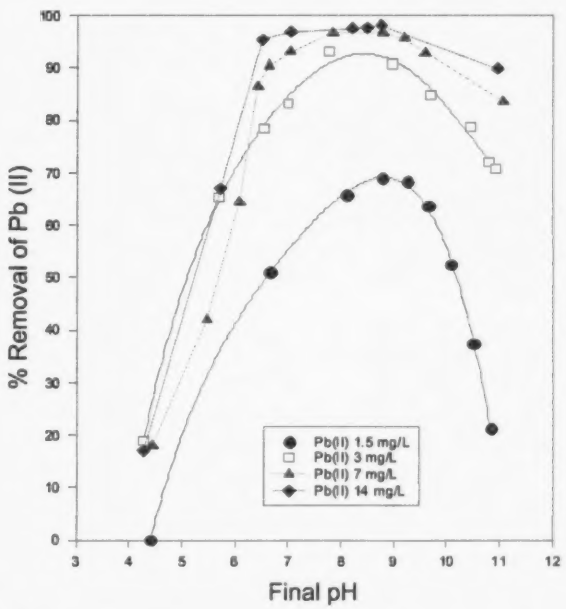

Fig.1. Percentage removal of Pb(II) at different pH in the absence of coagulant.

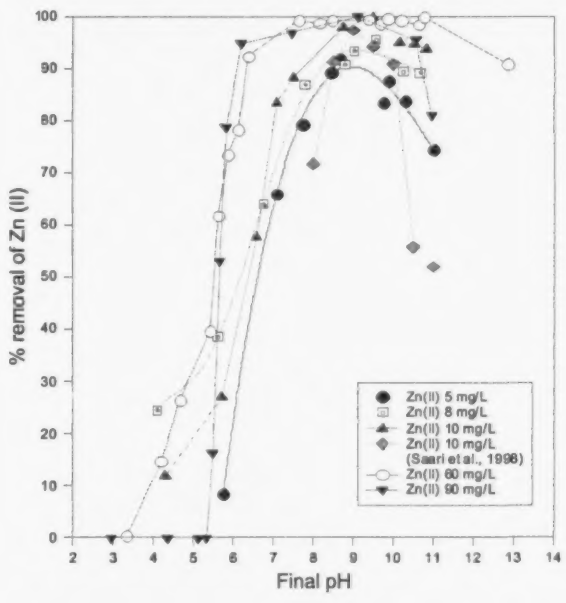

Fig.2. Percentage removal of Zn(II) at different pH in the absence of coagulant.

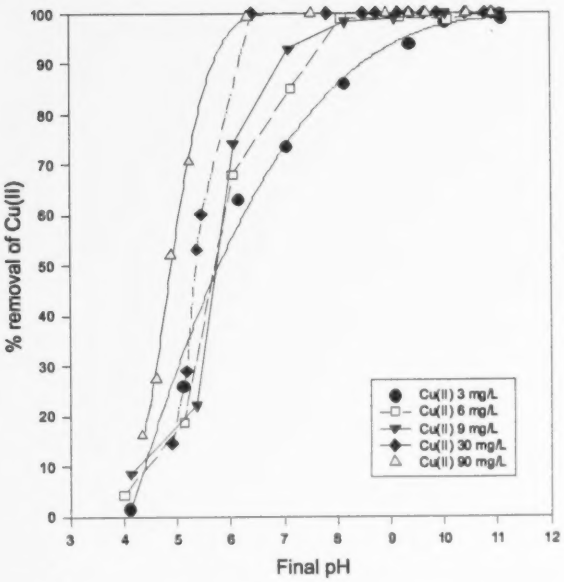

Fig.3. Percentage removal of Cu(II) at different pH in the absence of coagulant.

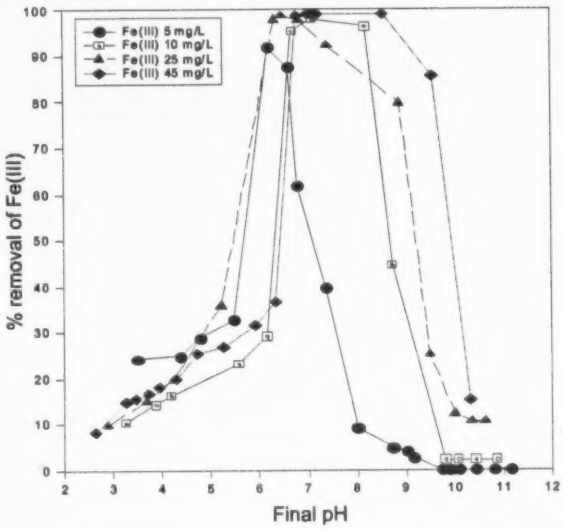

Fig.4. Percentage removal of Fe(III) at different pH in the absence of coagulant.

solutions fulfilled the standard discharge limit for all the three initial concentrations.

Generally, the percent removals of Cu(II) with initial concentrations of 3 to 90 mg/L by means of chemical precipitation are relatively high (≥99%) as shown in Fig. 3. The effective pH range for the best Cu(II) removal occurred from 8.1 to 11.1 for the initial concentrations of 3, 6, and 9 mg/L of Cu(II). This pH range agrees with the value of Baltpurvins et al. (1996). When the Cu(II) concentration increased to 30 and 90 mg/L, the effective pH range became broader (i.e., pH 6.3 to 11.1), and the final concentration of Cu(II) in the solutions was <0.2 mg/L, thus meeting the standard A discharge limit.

Figure 4 shows the plot of the percent removal of Fe(III) as a function of the solution pH at initial concentrations of 5, 10, 25, and 45 mg/L of Fe(III). It shows that the optimal pH range for Fe(III) removal occurred at a lower pH as compared with the other three heavy metals. The optimal pH range became wider when the initial concentration of Fe(III) increased from 5 to 45 mg/L. For an initial concentration of 5 mg/L Fe(III), the optimal pH range was 6.2 to 6.6, while for the other concentrations, the optimal pH range was 6.7 to 8.6. The optimal pH ranges obtained are similar to those of Hautala et al. (1977). Iron is soluble in acidic solution, but as the pH rose, Fe(II) and Fe(III) were converted into their respective hydroxides. According to Hautala et al. (1977), there was sufficient dissolved oxygen to oxidize Fe^{2+} to Fe^{3+} in a dilute neutral solution of iron (50 ppm or less). It was then assumed that probably only the Fe(III) species existed in the prepared solutions. Neutralization of an acidic iron solution with NaOH resulted in the precipitation of $Fe(OH)_3$. The precipitate was slow to settle and easily redispersed by slight agitation. The percent removal of Fe(III) in the alkaline zone was very poor. Beyond a pH of 9, there was almost no Fe(III) removal from the solution of lowest concentration. In this region, percent removal of Fe(III) increased with the concentration of Fe(III) . The percent removals of Fe(III) were 2.2, 25.0, and 85.5% for the initial concentrations of 10, 25, and 45 mg/L of Fe(III), respectively.

At pH corresponding to the minimum solubility, all metals form slightly soluble, gelatinous hydroxides in the presence of equivalent quantities of hydroxide ions, but the hydroxide precipitates may redissolve in water after the minimum solubility point by forming soluble anionic hydroxyl complexes because of amphoteric effects (Maruyama et al. 1975; Saari et al. 1998).

The percent removal of metal increased with initial metal concentrations, as shown in Fig. 5. This is in agreement with the findings of Daniels (1975) and Ayoub et al. (2001) who reported that higher influent metal concentrations result in greater metal removal. It was also found that each heavy metal experienced different removal efficiencies by hydroxide precipitation, which is probably due to its hydroxide solubility properties as well as affinity toward precipitating suspended solids.

The Effect of Coagulants on Pb(II) Removal

Chemical precipitation of the heavy metals of different initial concentrations showed that only Pb(II) needed further treatment after the hydroxide precipitation process in order to further reduce the final concentration of Pb(II) in the wastewater. The results of the alum, PACl, and $MgCl_2$ coagulation experiments of various coagulant

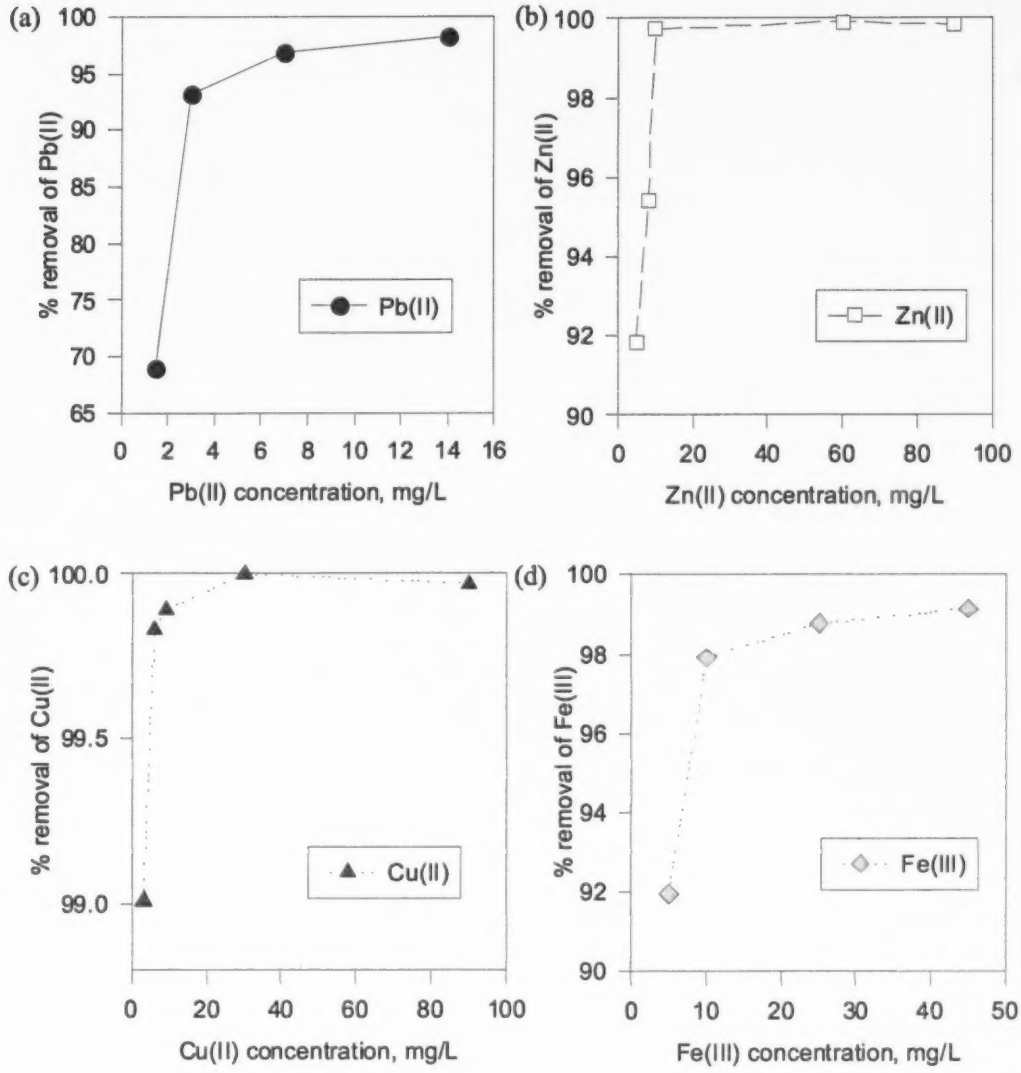

Fig.5. Percentage removal of metal as a function of metal initial concentrations. (a) Pb(II); (b) Zn(II); (c) Cu(II) and (d) Fe(III).

dosages on synthetic wastewater containing 7 mg/L of Pb(II) are shown in Fig. 6, 7, and 8, respectively. Upon the addition of coagulant to the alkaline solutions, metal removal was enhanced significantly. Fig. 6 shows that treatment with alum dosages of 1,200, 2,000, and 4,000 mg/L worked well to give >99% removal in the pH range of 6.9 to 8.0. Final concentrations of Pb(II) in the solutions were 0.038, 0.028, and 0.020 mg/L, respectively, which are lower than the Standard A discharge limit.

Figure 7 shows the use of PACl with excellent percent removal for almost all the dosages studied. For the initial concentration of Pb(II) (7 mg/L), percent removal as high as 98.6% needed to be achieved in order to meet the discharge limit. The corresponding pH range for the effective Pb(II) removal (>99%) was 8.1 to 8.9 when 150 mg/L of PACl was used. When the PACl dosage increased to 600, 800, and 1,200 mg/L respectively, the optimum pH range for the 99% removal became broader (i.e., 7.6 to 9.1) and the solutions contained only a small amount of Pb(II), which complied with the Standard A discharge limit.

The results of the jar tests with 7 mg/L of Pb(II) treated with $MgCl_2$ in a pH range of 9.0 to 12.5 are presented in Fig. 8. It shows that a higher coagulant

dosage is needed to remove 99% of Pb(II). $MgCl_2$ dosages of 600, 1,200, 2,000, 4,000, and 6,000 mg/L gave 92.6, 96.6, 99.4, 98.9, and 98.7% removal, respectively. It was observed that the pH for the maximum percent removal shifted slightly to the lower range when the $MgCl_2$ dosage increased. This is in agreement with the findings of Lefers et al. (1987), who showed that the pH value at which the precipitation of $Mg(OH)_2$ flocs starts depends on the Mg^{2+} concentration in the wastewater. This pH value decreased with increasing Mg content in the wastewater. Therefore, the treatment of wastewater containing relatively high concentration of Mg can be carried out at lower pH values.

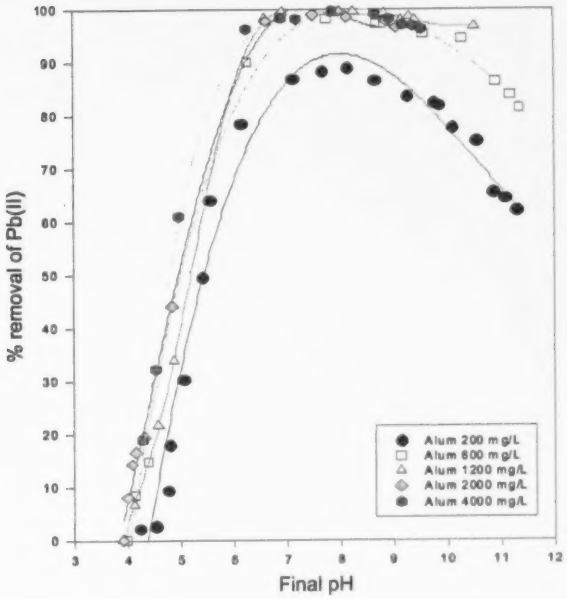

Fig.6. Treatment of 7 mg/L of Pb(II) with different alum dosages.

Figure 9 shows the percent of Pb(II) removal by various coagulants as a function of the coagulant dosage. The curves were drawn in different optimal pH ranges of 6.5 to 7.8, 8.1 to 8.9, and 9.7 to 10.9 for alum, PACl, and $MgCl_2$, respectively. For alum and PACl, the results showed that increasing the concentration of the coagulant increaseed the efficiency of the Pb(II) removal. The percent removal of Pb(II) increased with the increase of the coagulant dosage up to a limit, after which the percent removal attained an almost constant value. An almost similar removal efficiency for different dosages of coagulants means that the concentration of the coagulants remaining in the solution is higher, which may contribute to toxicity (Stephenson and Duff 1996).

The percent removal of Pb(II) increased from 89.0 to 98.1% when the alum dosage increased from 200 to 600 mg/L. A removal of Pb(II) higher than 99% can be attained by the addition of 1,200 mg/L of alum. The percent removal of Pb(II) was found to be >99% as the PACl dosage was increased from 150 mg/L to higher dosages. A complete Pb(II) removal was achieved when 800 and 1,200 mg/L of PACl were used. In the case of treatment with $MgCl_2$, precipitation with NaOH in a pH range of 9.8 to 10.5 in the absence of $MgCl_2$ was insufficient to achieve good removal of Pb(II). The

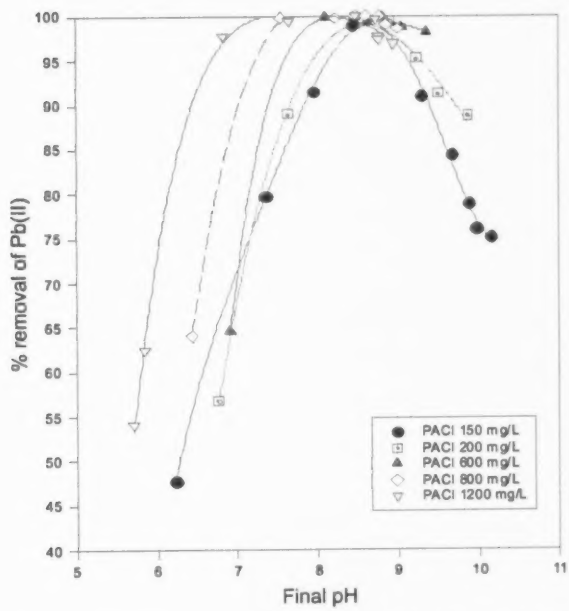

Fig.7. Treatment of 7 mg/L of Pb(II) with different PACl dosages.

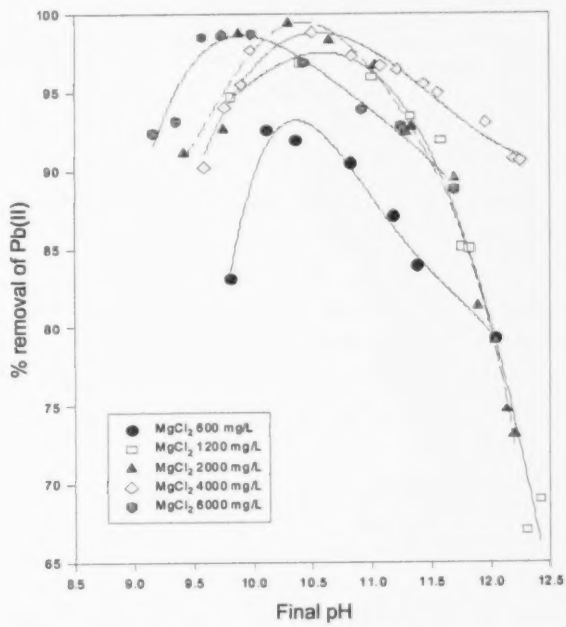

Fig.8. Treatment of 7 mg/L of Pb(II) with different $MgCl_2$ dosages.

final concentration of Pb(II) in the solution was 0.562 mg/L (i.e., 91.9% removal). $MgCl_2$ dosages of 600 and 1,200 mg/L exhibited lower percent removal of Pb(II) compared with alum and PACl at the same dosages. However, a $MgCl_2$ dosage of 2,000 mg/L gave almost the same percent removal (i.e., 99.4%) as an alum dosage of 2,000 mg/L (i.e., 99.6%). Further increase of the $MgCl_2$ to 4,000 and 6,000 mg/L slightly decreased the percent removal. This may be due to the restabilization of the colloidal particles by the excess $MgCl_2$ hydrolysis species, and therefore the Pb(II) ions remained in solution (Chu 1999).

Among the three coagulants used, PACl, which gives almost 100% removal of Pb(II) at a dosage of 150 mg/L, exhibited better removal efficiency than alum and $MgCl_2$. Less PACl was needed than alum and $MgCl_2$ to achieve the desired heavy metal removal. It has been reported that PACl has a few superior characteristics, including stronger metal removal ability than alum (Van Benschoten and Edzwald 1990; Sonu et al. 1997; Fan et al. 2003). In the presence of an aluminum-based coagulant, Al will remain as a "free ion" in acidic solutions. When the pH of the solution increases, the Al in PACl will form polymerized aluminum hydroxide, which provides a larger surface area over alum for Pb(II) to be adsorbed onto, and to trap the $Pb(OH)_2$ particles (Stephenson and Duff 1996; Chu 1999).

The Effect of the Coagulant Aid on Flocs Settling Time

Prior to the addition of the coagulant aid to the solutions, the tiny particles are dispersed in the solution and it takes a long time for the particles to settle down. The use of a coagulant aid greatly improves the flocs separation performance by promoting the growth of agglomerates of fine particles of such size and density that effective solid-liquid separation can be accomplished (Ødegaard 1987). The effect of polyelectrolyte on flocs settling time was studied on the 7 mg/L of Pb(II) aqueous solutions at the corresponding optimal coagulant dosage and pH value. The results displayed in Fig. 10 show that the settling time of the flocs treated with alum, PACl, and $MgCl_2$ with 0.5 mL of Koaret PA 3230 were 60, 81, and 569 s, respectively. The shortest settling time of the flocs treated with alum and PACl was about 31 s when 2.0 mL of Koaret PA 3230 was added to the solutions. Varying the amount of coagulant aid does not have the significant effect for the treatment by alum and PACl as they could easily settle in a short time. This is in good agreement with the result of Amokrane et al. (1997), who reported that the coagulation-flocculation process using alum as a coagulant and an anionic polymer as the coagulant aid provided flocs of greater size and lower sedimentation time. For the solutions treated by $MgCl_2$, the settling time decreased when the amount of coagulant aid increased. This shows that in order to bring down the settling time to about 100 s when $MgCl_2$ is used, a minimum amount of 5 mL of coagulant aid must be used.

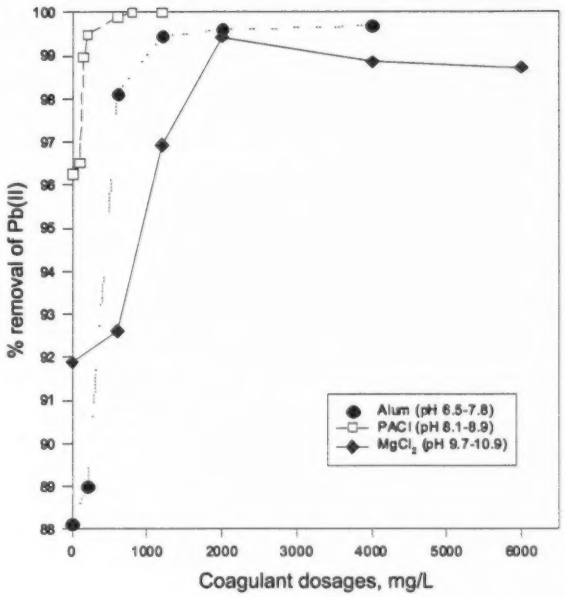

Fig.9. Effect of the use of different coagulants on the removal of 7 mg/L of Pb(II).

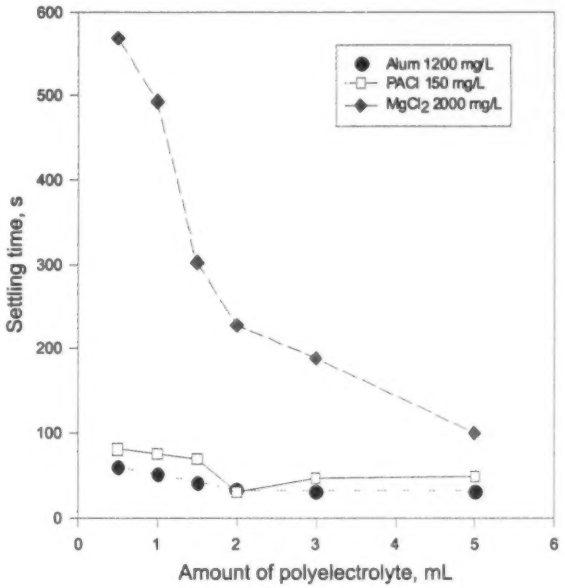

Fig.10. Flocs settling time as a function of amount of polyelectrolyte used.

Conclusions

The removal efficiency of heavy metals by hydroxide precipitation increased with increased metal concentration. Optimal removal of metals by hydroxide precipitation was attained at a fixed pH, which varied with the type

of metal. Individual Zn(II) and Cu(II) of concentrations below 90 mg/L and Fe(III) of concentration 45 mg/L in aqueous solutions were removed well by the precipitation method in the pH ranges of 8.7 to 9.6, 8.1 to 11.1, and 6.2 to 7.1, respectively. Alum, PACl, and $MgCl_2$ at dosages 1,200, 150, and 2,000 mg/L could achieve up to 99% removal for Pb(II) with an initial concentration of 7 mg/L at a pH range of 6.5 to7.8, 8.1 to 8.9, and 9.7 to 10.9, respectively.

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Electrochemical Removal of Copper and Lead from Industrial Wastewater: Mass Transport Enhancement

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The effects of ultrasonic frequencies on both the mass transport process and diffusion layer were investigated during electrochemical treatment. The rates of mass transfer at a stainless steel cathode were measured for copper and lead in dilute acidified copper sulphate and lead nitrate solutions at different ultrasonic frequencies. Concentrations in bulk solution were determined by atomic absorption spectrophotometer. By increasing frequencies from 40 to 100 kHz, a high value for the mass transfer coefficient and an effective thinning of the diffusion layer were observed. Higher rates of mass transfer reduced energy consumption. Use of ultrasound with electrochemical processes can provide valuable contributions to remove metallic ions from industrial wastewater without using extra chemicals. The process has efficiently reduced the cost of energy consumption and deposition time.

Key words: **electrochemical, ultrasound, heavy metal, mass transfer, diffusion layer**

Introduction

Wastewater from different industrial sectors (such as electroplating, photographic development, and printed circuit board production or battery technology) requires treatment to remove toxic metal ions and recycle valuable material. Due to increasingly strict regulations for the discharge of effluents, the permissible concentration of metal ions has been strongly decreased in recent years (Kreysa 1988; Kreysa et al. 1994). The removal of toxic ions from wastewater is a challenge since they are difficult to remove by biodegradation. Furthermore, some heavy metals like Pb, Cu, Hg, and Cr inhibit or prevent the oxidation of organic waste by bacteria (Bourgeois et al. 2001).

The use of an electrochemical approach to remove metal ions from wastewater can be considered a relatively simple and clean method. In many cases the technique is found to be superior to other techniques, such as chemical precipitation, ion exchange, and cementation (Genders and Weinberg 1992; Rajeshwar and Ibanez 1997; Juttner et al. 2000). But there is still a need to increase the mass transfer rate and reduce deposition time. The combination of ultrasound and electrolysis is commonly used in a wide range of subject areas such as electrode-position, electroplating, and for preventing corrosion and electrochemical dissolution (Walker 1993; Walton 1996; Compton et al. 1997a, 1997b).

Use of ultrasonic agitation for mass transfer is well known in electroplating; ultrasound accelerates the transfer processes of nickel and copper (Kobayashi et al. 2000; Kobayashi et al. 2001; Farooq et al. 2006). Each point in the liquid is subjected to alternating negative and positive pressure, which creates cavitation bubbles and subsequent implosion. This implosion creates a tiny but intense area of pressure and temperature, which reduces the diffusion layer (δ) of the electrochemical reaction (Richard and Joel 2002). Many of the observed effects of ultrasound in electrochemical processes can be explained by the enhancement of mass transport in diffusion-controlled processes. Sonication is believed to decrease the diffusion layer thickness thereby giving a substantial increase in the limiting current. The objective of the present study was to remove metals from model metal solutions, and to investigate the effect of ultrasound on the mass transfer rate of copper and lead.

Materials and Methods

Experiments

All experiments were performed with the Digital Ultrasonic Bath (Cleaner Model Utech Products, Inc.) at 40, 60, 80, and 100 kHz ultrasonic frequencies in a rectangular perspex glass vessel. Sonication was produced parallel to the liquid surface and the electrodes were hung vertically in the solution. Couples of stainless steel cathode and titanium anodes were used for the deposition of metallic ions. The surface area of the electrodes that were dipped into 1 L of solution was 102 cm^2. Electrodes were connected to the DC power supply (Dazheng PS-305D) with a digital current and voltage display. The experiments were conducted for 4 hours at 10 volts.

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Solutions

Model solutions were prepared in the lab with analytical grade salts of copper sulphate ($CuSO_4$) and lead nitrate [$Pb(NO_3)_2$]. The pH was adjusted by using 0.1-molar sulphuric acid.

Measurements

Mass transfer measurements were characterized by electro-diffusional method (Touyeras et al. 2005). The mass transfer coefficient, K_m, was calculated as follows:

$$K_m = I_{lim}/nFAC_o \quad (1)$$

where I_{lim} is the limiting current (A); F is the Faraday constant (96,485); n is the number of electrons; A is the area of electrodes (m^2); and C_o is the concentration difference of electro-active substance (mol/m^3).

Electrical energy consumption (EC, in kWh/mg) was calculated according to equation 2:

$$EC = Pt/\text{weight deposited} \quad (2)$$

where P is the power in kWh (kilowatt hours), t is the time in hours, and deposited weight of metals is in milligrams. The concentrations of metals were determined using a PerkinElmer atomic absorption spectrophotometer.

Statistical Analyses

Data were analyzed by the two tailed t-test at p-value of 0.05.

Results and Discussions

Effect of Ultrasound on Mass Transfer Coefficient and Diffusion Layer

Electrochemical experiments were carried out chrono-amperometrically (the potential was maintained at a constant level and current was measured as a function of time) using aqueous solutions of 0.1-M $CuSO_4$ and 0.1-M $Pb(NO_3)_2$ at various ultrasonic frequencies (40, 60, 80, and 100kHz). The chemical change that takes place during the electrochemical process for copper and lead ions is:

$$Cu^{2+} + 2e^- \rightarrow Cu(s)$$
$$Pb^{2+} + 2e^- \rightarrow Pb(s)$$

The relationship between the limiting current (I_{lim}) and the diffusion layer thickness can be described by the well known equation (Marken et al. 1996; Compton et al. 1997a; Gutierrez et al. 1998; Ball and Compton 1999):

$$I_{lim} = nFADC_o/\delta \quad (3)$$

where n is the number of electrons, F is the Faraday constant (96,485), A is the area of electrode in the solution (m^2), D is the diffusion coefficient/diffusivity of the electro-active substance, C_o is bulk concentration of this electro-active substance (mol/m^3), and δ is diffusion layer thickness (m).

By comparing equations 1 and 3, we get that the diffusion layer thickness (δ) is the ratio between the diffusion constant and the mass transfer coefficient. The following equation (4) and Fig. 1a and 1b show the inverse relation between the mass transfer coefficient and diffusion layer thickness.

$$\delta = D/K_m \quad (4)$$

where D the diffusivity is calculated by the Cottrell equation (5) (Bard and Faulkner 2001). From the results it was found that the diffusion coefficients for Cu^{+2} and Pb^{+2} using aqueous solutions of 0.1-M $CuSO_4$ and 0.1-M $PbNO_3$ were $1.61 \times 10^{-6}\ cm^2 \cdot s^{-2}$ and $2.48 \times 10^{-6}\ cm^2 \cdot s^{-2}$. Bing and Ian (2004) measured an effective diffusion coefficient for Cu^{+2} using a rotating disc electrode from both the Cottrell and Levich equations. The Cottrell analysis provided a value for the effective diffusion coefficient at bulk composition and viscosity (Bing and Ian 2004).

$$I_{lim} = nFAC_o(D/\pi t)^{1/2} \quad (5)$$

Figure 1a shows an increase in the mass transfer coefficient (K_m) for Cu as ultrasound frequency was increased to the maximum frequency of 100 kHz ($K_m = 1.21 \times 10^{-2}$ m/s) from the silent condition ($K_m = 0.67 \times 10^{-2}$m/s). Similarly, in the case of Pb, Fig. 1b shows an increasing trend, and at 80 kHz a high value ($K_m = 1.6 \times 10^{-2}$ m/s) was found in comparison with the silent condition ($K_m = 0.68 \times 10^{-2}$ m/s).

These results can be explained as a mass transfer effect at the electrode (Walker 1993; Klima et al. 1994; Walton 1996; Compton et al. 1997b), which is due to acoustic streaming, cavitation, and/or microstreaming in the bulk solution, and has an important role in the effective thinning of the diffusion layer, as shown in Fig. 1a and 1b. Marken et al. (1995) stressed that the dominating effect of ultrasound is strongly enhanced mass transport, resulting from a very thin diffusion layer thickness. He neglected the contribution of a transient component on the limiting current. He observed that the mass transfer was enhanced near the electrode surface.

Before initiating electrolysis, the concentration of metal ions is uniform throughout the solution. The concentration of metal ions near the electrode surface becomes less than the bulk solution because, when current flows through the solution, the surface of the particles becomes charged and some ions of the opposite charge become attached to their surface. The ions are held there through electrostatic and van der Waals forces of attraction, forming a fixed layer of ions surrounded by a diffuse layer, which stops the diffusion of metallic ions towards the electrodes (Metcalf and Eddy 2003).

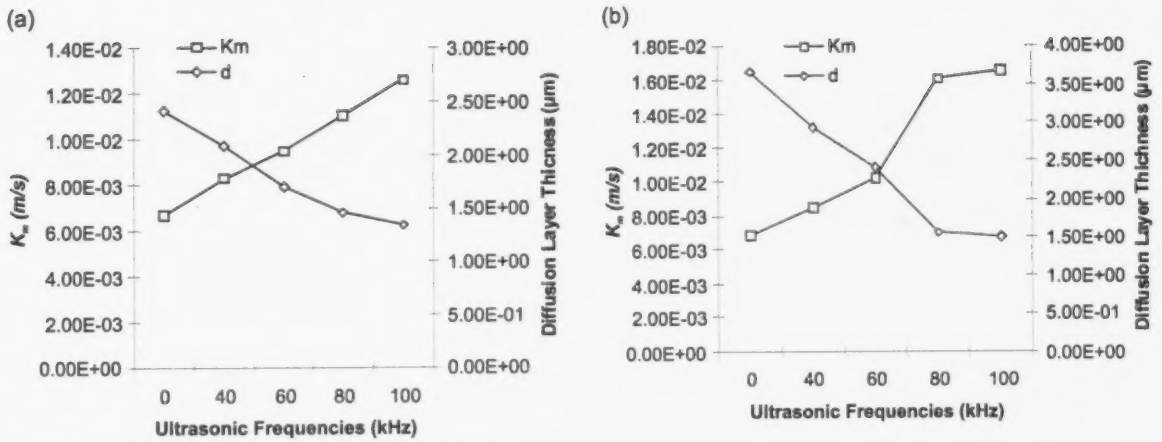

Fig. 1. Effect of ultrasonic frequencies on mass transfer coefficients and diffusion layer thickness for Cu (a) and Pb (b) during the first hour of the experiment.

The most important mass transport processes in an electrochemical measurement are diffusion and forced convection. At low concentrations of solutions, the only way in which metallic ions can be transported across the boundary layer to the electrode is by diffusion (Farooq et al. 2006). The rate of diffusion is increased by the application of ultrasound. The direct effect of ultrasound on mass transfer can arise due to three major mechanisms: acoustic streaming, microstreaming, and microjetting. Basically, acoustic streaming arises from attenuation of the sound field within the liquid, resulting in a pressure gradient and subsequent liquid motion. Microstreaming occurs close to a forced oscillating bubble or some other vibrating body. Microjetting occurs when a cavitation bubble collapses asymmetrically next to a solid/liquid interface (Wang and Jepson 2000).

Effect of Temperature and pH

The temperature of the solution was adjusted at 25°C, but during the experiment, temperature was increased accordingly with the intensity of the ultrasound, as shown in Fig. 2. An increase in temperature depends upon the collapse of acoustic cavitation in the solution (Farooq et al. 2003). On collapse, a high temperature and pressure are produced. The frequency of the ultrasound also affects the creation of cavitational bubbles; more bubbles are produced at higher frequencies (Banks and Compton 2004). The temperature increase also enhanced the deposition rate because of the degree of dissociation of the electrolyte. The viscosity of the electrolyte decreases at higher temperatures; therefore, the diffusion rate and the velocity of the copper ions and inhibitor molecules become increased.

Electrolytic removal of Cu and Pb was also studied at different pH conditions; the optimum pH range was 3 to 3.5 in the presence of ultrasound. A high concentration of hydrogen ions also increases the flow of current in the solution, which leads to an increase in the mass transport rate at the cathode, and a decrease in the diffusion layer thickness (Tables 1 and 2). However, a pH below 3 corrodes the electrode and reaction vessel.

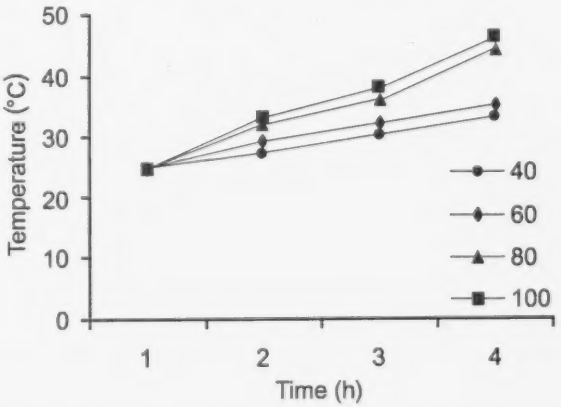

Fig. 2. The effect of ultrasonic frequencies on temperature.

TABLE 1. Effect of different pH conditions on mass transfer coefficient (K_m) and diffusion layer thickness (δ) for Cu

	pH				
	2	*2.5*	*3*	*3.5*	*4*
K_m (m/s)	1.44×10^{-2}	1.32×10^{-2}	1.21×10^{-2}	1.16×10^{-2}	0.98×10^{-2}
δ (µm)	1.08	1.28	1.34	1.46	1.59

TABLE 2. Effect of different pH conditions on mass transfer coefficient(K_m)and diffusion layer thickness (δ) for Pb

	pH				
	2	*2.5*	*3*	*3.5*	*4*
K_m (m/s)	1.77×10^{-2}	1.68×10^{-2}	1.60×10^{-2}	1.56×10^{-2}	1.37×10^{-2}
δ (μm)	1.34	1.51	1.55	1.62	1.73

Effect of Ultrasound on Removal of Metals

Figures 3 and 4 reflect the effect of different ultrasonic frequencies during electrolytic removal of Cu^{2+} and Pb^{2+} at a steel cathode and constant voltage of 10 volts. A pH of 3 was maintained during all experiments. Temperature increased from 25 to 45°C due the collapse of cavitational bubbles. The initial concentrations of copper and lead used were 25 and 32 mg/L, respectively.

On the basis of the test applied, it is evident that our data are significantly different from the preceding treatment ($p < 0.05$). As seen from Fig. 3 and 4, the deposition of copper and lead increased rapidly in the first hour with the increase of frequency. At the frequencies of 80 and 100 kHz, 99% removal of metals in 4 hours was observed. Farooq et al. (2006) also found a high percentage of Cu^{+2} removal and a decrease in current efficiency by application of ultrasound in the electrolysis process. The deposition rate decreased with the passage of time (Fig. 3 and 4), due to the decrease in concentration gradient and the decrease in conductivity of the solution. Conductivity in wastewater is due to the presence of ions in the solution. As the electrochemical process proceeds, the ions are either converted into metallic atoms or into gases (Silberberg Chemistry 2003). The concentration of Cu at 100 kHz decreased from 25 to 8.4 ppm in 1 h, but in a simple electrolysis process, the concentration decreased from 25 to 15.1 ppm. Hence, the addition of ultrasound increased the mass transport at the electrodes. At extremely low concentrations, the rate of the mass-transport-controlled process strongly decreases (Juttner et al. 2000).

It was observed that energy consumption varied with the deposition rate. The flow of current through aqueous solutions depends upon the concentration of positive and negative ions in the solution, and the voltage applied. High concentration of ions increased the current through the solution. Since the concentration of metallic ions in the dilute solution was low, the voltage applied from the battery was 10 volts, which gave the desired current flow. High current flow and high voltage also increase the current density as well as operating costs (Walton 1996), but, by applying ultrasound, this cost can be reduced at the same current flow and voltage. Low energy consumption during the ultrasound electrolysis process was noticed.

The percentage removal of Cu in the simple electrolysis process was 67.2%, with a high electrical consumption of 0.053 kWh/mg in four hours (Table 3). However, with the increase of frequency from 40 to 100 kHz, the rate of Cu removal was increased with a consequent decrease in energy consumption compared with the simple electrolysis process. At the frequency of 40 kHz, Cu removal was 65.8% with an energy consumption of 0.046 kWh/mg in 3 h. Similarly, 68.8% removal was found at the 60 kHz frequency after 2 h, with an electrical consumption of 0.033 kWh/mg. At 80 and 100 kHz, 67.8% Cu removal was found with an electrical consumption of 0.018 kWh/mg, which is one third of the consumption seen using the simple electrolysis process. Similar results were observed during the removal of Pb from the solution.

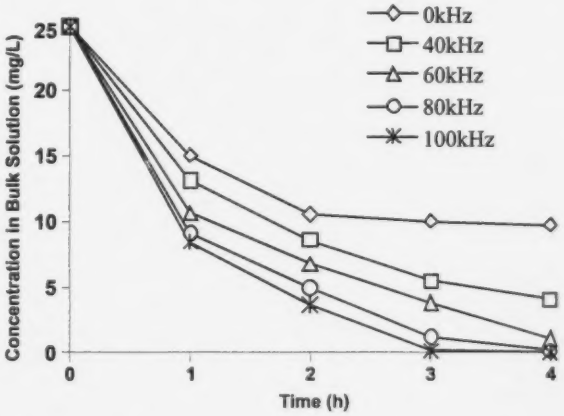

Fig. 3. Effect of ultrasonic frequencies during electrolytic removal of copper from its solution.

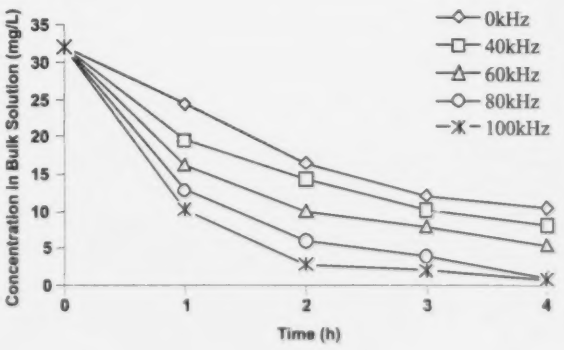

Fig. 4. Effect of ultrasonic frequencies during electrolytic removal of lead from its solution.

TABLE 3. Energy consumption of Cu and Pb at different ultrasonic frequencies

	Time (h)	0 kHz		40 kHz		60 kHz		80 kHz		100 kHz	
		EC[a,b]	Removal[b]	EC	Removal	EC	Removal	EC	Removal	EC	Removal
Cu	1	0.026	35.8	0.024	44.2	0.019	54.8	0.016	61.2	0.014	64.2
	2	0.026	55.2	0.036	60.5	0.027	71.1	0.025	78.8	0.021	83.0
	3	0.031	62.0	0.043	76.7	0.037	83.8	0.032	95.1	0.030	99.4
	4	0.037	64.0	0.051	82.6	0.047	95.7	0.039	98.6	0.038	99.9
Pb	1	0.021	24.1	0.025	39.1	0.021	49.1	0.019	59.4	0.018	67.8
	2	0.028	48.8	0.038	55.0	0.033	68.7	0.030	78.7	0.028	90.6
	3	0.041	62.1	0.046	65.8	0.042	75.3	0.038	87.5	0.036	93.7
	4	0 053	67 2	0 057	74 4	0 050	82 8	0 048	98 8	0 048	98.0

[a] EC = energy consumption.
[b] Units: EC, kWh/mg; Removal, %.

Significance of the Study

In Pakistan, industries discharging heavy metals include the electroplating, battery, and ghee industries, as well as tanneries. Electrolytic removal of metals can be beneficial in terms of a reduction in cost of chemicals used for the precipitation (Sirajuddin et al. 2004; Farooq et al. 2006; Sirajuddin et al. 2007). Also, precious metals can be efficiently removed from their ores using electrolytic removal. Table 4 shows characteristics of the ghee and battery industries as well as tanneries. Electrolytic recovery of nickel from the solid waste of hydrogenated vegetable oil, called ghee waste, was studied by Sirajuddin et al. (2004). They found 200 ppm of nickel in the ghee waste. Sirajuddin et al. (2007) studied the electrolytic recovery of chromium from tannery effluents.

TABLE 4. Characteristics of different industrial effluents

Parameters	Effluent		
	Ghee	Battery	Tannery
Ni (ppm)	20	—	—
Pb (ppm)	—	30	—
Cu (ppm)	—	0.04	—
Cr^{+3} (ppm)	—	—	1,000
COD (ppm)	255	—	1,760
pH	7.5–8	6	8–9
TDS (ppm)	965	300	5,260
Conductivity	1,930 µS	605 µS	10–12 mS

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Electrokinetic Flotation of Process Water from Paint Booths

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Electrokinetic flotation (EKF) for separation of paint solids and process water from automotive assembly paint booths was investigated in a series of laboratory-scale batch experiments. The EKF process employs a single electrode-module and a DC (direct current) power supply, but does not use any chemical agents or air supplier. The electrode-module, which consists of parallel electrode plates, was developed and used in the experiments. The influencing parameters of the EKF process for the process water treatment, including the type of paint, initial suspended paint solids (SS) concentration, and applied electric current, were investigated in the experimental program. It was found from this study that the EKF process decreased the SS concentration from 300 to 100 mg/L in 30 minutes at 55 A/m² in the water-borne paint water, from 150 to 50 mg/L in 5 minutes at 22 A/m² in the solvent-borne paint water, and from 550 to 100 mg/L in 5 minutes at 44 A/m² in the mixed paint water, as well as reduced colour and chemical oxygen demand (COD). The study concluded that paint type, initial SS concentration, and electric current are the most important parameters in the EKF process governing the effectiveness of solid/water separation, treatment time, and power consumption. A comparison of SS removal between the chemical coagulation and the EKF treatments showed that SS removal by the EKF process was similar to the chemical treatment. The study concluded that the EKF is an effective technique for solid/water separation in paint booths with simultaneous COD and colour removal.

Key words: **electrokinetic flotation, industrial process water treatment, paint spray operation, suspended solids, solid/water separation.**

Introduction

Chemical coagulation of process water is extensively used in automotive paint booths to separate oversprayed paint from water (Collins et al. 1991; Haas TCM 2007; Milanco Industrial Chemicals 2007). The chemical coagulation of paint process water involves the application of large quantities of chemicals, such as coagulants, detackifier, biocide, deformer, and caustic soda (Collins et al. 1991; Kia et al. 1993, 1996, 1997). As a result, suspended particles either settle in the sludge zone of the treatment tank by gravitational settling, or float on the surface of the water body by air bubbles (Metcalf and Eddy 1991; Droste 1997; Rubio et al. 2002). The separated sludge is mechanically collected and removed for further treatment and disposal.

The automotive industry generates a lot of waste paint sludge. For example, about 34,000,000 kilograms of waste paint sludge is generated by the U.S. automotive industry each year (Sanghvi and Massingill 2002). This waste makes a significant contribution to landfills and presents an environmental danger through the discharge of toxic materials to the environment. The use of recovered paint overspray from the automotive industry has been investigated. For example, approximately 80% of latex and alkyd waste paint could be recovered by mechanical sorting and segregation of paint and converting it into safe, quality recycled paint products (Sanghvi et al. 2002). The results indicate that the recycled paint gave reasonable properties for many expected industrial applications. Therefore, efforts to reduce chemical usage and the amount of paint sludge generated may be beneficial in terms of paint sludge recovery and environmental protection.

Air flotation combined with chemical coagulation techniques are commonly employed in the solid/water separation process when the specific gravity of suspended particles is lower or close to that of water (Arora et al. 1995; Edzwald 1995; Fukushi et al. 1995; Vlaski et al. 1997; Voronin and Dibrov 1998; Haarhoff and Edzwald 2001; Han et al. 2001; Al-Shamrani et al. 2002; Rubio et al. 2002; Ljunggren and Jonsson 2003). However, these processes have several disadvantages on process water treatment in automotive assembly paint booths: (1) chemical preparation, device operation and maintenance, as well as chemical transportation and storage are costly and time consuming; (2) the type of chemical and its dosage need to be closely monitored and routinely tested to ensure system performance, which further increases operation costs and affects treatment efficiency; (3) chemicals added in the process water of paint booths are nonrecoverable and increase the mass and volume of paint sludge generated in the process, and as a result, lead to increased cost of sludge dewatering and disposal as well as difficulties in sludge recycling and reuse; (4) many

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of the chemicals used in the process are water-soluble organic solvents and will remain in the process water, and, as a result, have impacts when the process water is discharged, particularly when there is a strict limit to the amount of organic matter discharged (Kia et al. 1996).

Electrokinetic flotation (EKF) is a solid/water separation process that floats suspended particulate pollutants to the surface of a water body by electrochemical effects, such as the generation of tiny bubbles of hydrogen (H_2) and oxygen (O_2) gases from water electrolysis (Fukui and Yuu 1980, 1985; Hosny 1992; Chen 2004), and other effects associated with electrokinetics, including changes of the particle surface charge due to DC (direct current) and anode consumption. The EKF process enhances flotation efficiency and reduces or eliminates chemical dosage (Koren and Syversen 1995; Chen 2004; Ibrahim et al. 2001; Kolesnikov et al. 2001; Murugananthan et al. 2004). The EKF process is especially suitable to small-scale water and wastewater treatment, such as in the separation of lightweight and extra-fine sized solids from water during industrial process water treatment (Hosny 1992, 1996). The EKF technique has reached a state that is not only comparable with other techniques in terms of cost, but is also more efficient and more compact (Burns et al. 1997).

In this study, the EKF technique for the treatment of process water from paint booths was studied in order to improve treatment efficiency, including the control of suspended solids (SS) concentration, colour, and chemical oxygen demand (COD) accumulation, and the reduction of paint sludge, including sludge volume and extra chemical components that were created from chemical coagulation. This paper presents a laboratory-scale EKF performance evaluation on solid/water separation of process water in paint booths. One water-borne paint and two solvent-borne paints were used to prepare paint water samples. The type of paints, initial concentration of SS, and applied direct current were studied in real time. In addition, chemical coagulation and EKF were compared in order to demonstrate the effectiveness of the EKF process.

Materials and Methods

Synthetic Paint Water

The synthetic paint water sample (i.e., a water-borne base coat water, a solvent-borne primer, a solvent-borne clear coat water, and a mixed paint water) were prepared using three types of paints and chemicals, which were supplied by an automotive assembly plant. The types of paints were a water-borne base coat, a solvent-borne primer, and a solvent-borne clear coat. The chemicals included a detackifier and sodium hydroxide solution (NaOH, 30 to 60%). The control parameters for the preparation included the paint type, SS concentration, chemical type and dosage, pH, electric conductivity, and particle size. A gravity fed air spray gun with regulator (GRIP-13140 HVLP Air Spray Gun) was used to spray paint into water. In addition, the mixed paint water was prepared using the above three types of paint waters in a volumetric ratio of 1:1:1. The operation procedure for the preparation is described in Table 1.

The characteristics of the synthetic paint waters are summarized in Table 2. The water-borne paint water (base coat water) had a pH of around 7.0, while the solvent-borne paint waters (primer water and clear coat water) had pH values of 8.2 to 8.6. Paint solids suspended in water had the specific gravity (G_s) of 1.47 to1.52 and the negative zeta potential (ξ) of -16.0 to -24.0 mV. The detackifier to paint ratio (D/P ratio) and dosage of NaOH solution for the synthetic paint water preparation were based on the instructions used at the automotive assembly plant. The particle size distributions of the synthetic base coat water sample and the process water sample from the paint booths of the automotive assembly plant were measured for comparison. As shown in Fig. 1, both curves show two peaks of particle size in the range of 1 to 2 μm, and in the range of 15 to 20 μm, respectively. The mean particle size was 15 μm for the synthetic paint water sample (Fig. 1a), and 20 μm for the automotive process water sample (Fig. 1b). On the other hand, the percentage of particles finer than 20 μm was

TABLE 1. The procedure for the synthetic paint water preparation

Water-borne base coat water	*Solvent-borne clear coat and primer water*	*Mixed paint water*
1. Add tap water in an empty tank, 2. Add detackifier in the tank based on the detackifier to paint volumetric ratio of 1:10, 3. Spray base coat into the tank using the spray gun with 80 kPa air pressure, 4. Measure TS concentration, and 5. Adjust TS concentration by tap water.	1. Add tap water in an empty tank, 2. Adjust pH to 8.3 to 8.6 using NaOH solution, 3. Add detackifier in the tank based on detackifier to paint volumetric ratio of 1:7, 4. Spray clear coat or primer into the tank using the spray gun with 80 kPa air pressure, 5. Measure TS concentration, and 6. Adjust TS concentration by tap water.	1. Prepare base coat water (TS = 1,550 mg/L), clear coat water (TS = 4,600 mg/L) and primer water (TS = 2,374 mg/L), 2. Mix above three types of paint water by volumetric ratio of 1:1:1, and 3. Measure TS concentration.

TABLE 2. Characterization of the synthetic paint waters[a]

Type	*pH*	*κ (ms/cm)*	*Gs*	*ξ (mV)*	*D/P ratio*	*Chemicals*
Water-borne base coat water	6.9 to 7.2	0.25 to 0.32	1.47 to 1.52	-16.0 to -19.6	1/10	Base coat Detackifier Tap water
Solvent-borne primer water	8.2 to 8.6	0.25 to 0.32	1.47 to 1.52	-18.0 to -24.0	1/7	Primer Detackifier NaOH Tap water
Solvent-borne clear coat water	8.2 to 8.6	0.25 to 0.32	1.47 to 1.52	-18.0 to -24.0	1/7	Clear coat Detackifier NaOH Tap water

[a] κ: electric conductivity (ms/cm); Gs: specific gravity; ξ: zeta potential; D/P ratio: the ratio of detackifier/paint.

84% for the synthetic paint water sample and 53% for the automotive process water sample. Comparing Fig. 1a and 1b, the particle sizes of the synthetic paint water sample were smaller than those in the process water from the automotive assembly plant. Therefore, from the point of view of paint/water separation, there was much more difficulty with the synthetic paint water than with the automotive process water.

Electrokinetic Flotation Cell

The EKF cell, shown in Fig. 2a, was made of a plexiglass tube with a 5-mm wall thickness. The cell was 320 mm in effective height and 152 mm in inner diameter with 1.81 × 10^4 mm^2 in the sectional area. The effective volume of the cell was 5.6 L. A sampling port was equipped on the cell at 55 mm from the bottom of the cell. The electrodes are shown in Fig. 2b. The anode was made of 1.0-mm thick graphite plate, and the cathode was made of steel mesh (Flattened mesh, 35% of open area). The electrode-module was seated on the bottom of the flotation cell, which consisted of both anode and cathode plates arranged parallel to each other. In order to avoid electric short-circuit, a plastic mesh spacer with a height of 13 mm was inserted between the anode and cathode plates. The connection of electrodes to the DC power supplied was through 24 AWG cables. The current was applied via a DC power supply (Hewlett Packard 6545A, 0-120 V, 0-1.5 A) and monitored by two multimeters for current and voltage.

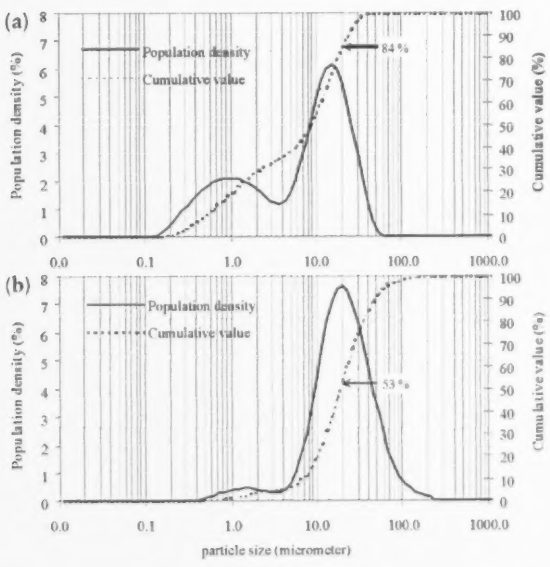

Fig. 1. Particle size distribution of water-borne base coat water: (a) synthetic paint water, (b) sample of automotive assembly plant.

Experiment

A series of lab-scale batch experiments were carried out using the four types of synthetic paint waters to evaluate the EKF process. SS, COD, colour, and pH were compared with flotation time. The relationship of contamination removal to applied current was closely investigated.

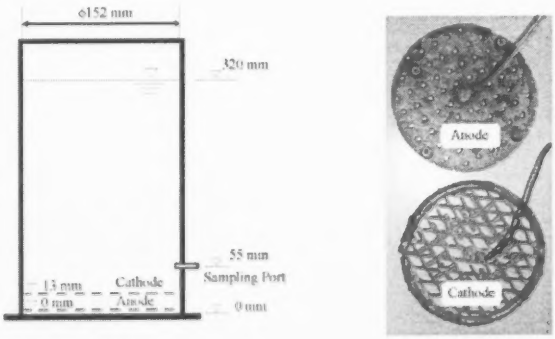

Fig. 2. Batch cell and electrodes for the EKF experiments.

Finally, the experiment demonstrated the efficiency of SS removal from different paint types, as well as compared SS removal between the conventional chemical treatment and the EKF treatment.

The synthetic paint water sample was transferred into the EKF cell using a siphon to avoid adding air bubbles to the water body; the EKF experiment started when the cell was filled to 320 mm (Fig. 2). Water samples were taken from the sampling port. The floated sludge was collected from the top of the cell after the experiment. Total solids (TS), SS, COD, and colour of the synthetic water samples were monitored. The applied current and voltage were on-line monitored by two multimeters. As soon as possible, the pH of the synthetic paint water sample was measured. TS, SS, COD, turbidity, and colour of the water samples, and solids concentration of the floated sludge samples were measured after each test. TS, SS, and COD measurement followed method 2540B, 2540D and 5220D in the *Standard Methods for the Examination of Water and Wastewater* (APHA et al. 1999). Turbidity and colour were measured by a spectrophotometer (DR 2000, Hach Company, U.S.A). Specific gravity measurement followed ASTM D1429-03, Test Method A – Pycnometer at 20°C (±1°C). The particle size distribution and zeta potential of the paint water were analyzed by a Mastersizer 2000 Particle Size Analyzer (ZetaPlus, Malvern Instruments Ltd. U.K.) and a Zeta Potential Analyzer (Brookhaven Instruments Corporation, U.S.A.), respectively.

The water quality of the synthetic water-borne base coat water samples and the applied current densities for the EKF experiments are summarized in Table 3. Three initial TS concentrations were prepared for the base coat water samples: 790 to 879 mg/L for run W-B1, 1,590 to 1,680 mg/L for run W-B2, and 2,950 to 3,340 mg/L for run W-B3. The applied current density was arranged from 0 to 65.8 A/m^2 with an increment of 11.0 A/m^2 under each TS concentration.

The water quality of the synthetic clear coat water samples, solvent-borne primer water samples, and mixed paint water samples, as well as the applied current densities for the EKF experiments are summarized in Table 4. Runs S-C1 and S-C2 represent the experimental conditions of the clear coat water, in which the TS concentrations were 1,992.0 and 4,669.3 mg/L, respectively. Runs S-P1 and S-P2 represent the experimental conditions of the primer water, in which the TS concentrations were 1,432.0 and 2,374.0 mg/L, respectively. Run M-M1 represents the experimental conditions of the mixed paint water, in which the TS concentration was 2,789.0 mg/L. The applied current density for the solvent-borne paint water and mixed paint water was arranged from 11.0 to 54.9 A/m^2 with an increment of 11.0 A/m^2 under each TS concentration.

The DC current was controlled as a constant for each EKF batch experiment and was delivered to the water body by the electrode-module. The current was calculated by:

$$I = i \cdot Area \quad (1)$$

TABLE 3. Experimental conditions of the water-borne base coat water

RunNo.	*Current[a] density (A/m^2)*	*TS (mg/L)*	*SS (mg/L)*	*COD (mg/L)*	*Colour (PtCo unit)*
W-B1	0–65.8	790–870	296–320	1,020–1,340	5,100–5,400
W-B2	0–65.8	1,590–1,680	596–636	3,120–3,420	9,200–9,650
W-B3	0–65.8	2,950–3,340	1,208–1,384	6,200–7,400	16,150–20,000

[a] The increment of current density is 11.0 A/m^2 in the range of 0 to 65.8 A/m^2.

TABLE 4. Experimental conditions of solvent-borne primer, clear coat and mixed paint water

Run No.[a]	*Current[b] density (A/m^2)*	*TS (mg/L)*	*SS (mg/L)*	*COD (mg/L)*	*Colour (PtCo unit)*
S-C1	11.0–54.9	1,992.0	562.9	2,260	78
S-C2	11.0–54.9	4,669.3	759.3	3,970	95
S-P1	11.0–54.9	1,432.0	155.6	1,120	129
S-P2	11.0–54.9	2,374.0	382.6	1,490	297
M-M1	11.0–54.9	2,789.0	562.4	2,770	255

[a] S-C*n*: solvent-borne clear coat water; S-P*n*: solvent-borne primer water; M-M*n*: mixed paint water.

[b] The increment of current density is 11.0 A/m^2 in the range of 11.0 to 54.9 A/m^2.

where, I was the applied current (A), i was the current density on the electrode module (A/m^2), and *Area* was the one-side surface area of the electrode plate (m^2). The current density was in the range from 0 to 65.8 A/m^2 with an increment of 11.0 A/m^2.

The percentage of SS removal was defined as:

$$\eta = \frac{c_1 - c_2}{c_1} \times 100\% \qquad (2)$$

where, η was the percentage of SS removal (%), c_1 was the initial SS concentration (mg/L), and c_2 was the SS concentration at a specific flotation time (mg/L).

The suspended paint solids in the process water from paint booths had typically small sizes, from 0.1 to 100 μm (see Fig. 1), and carried negative charges with zeta potentials lower than -16.0 mV. Therefore, chemical coagulation was often employed for solid/water separation. The chemical dosage required to achieve separation was related to many parameters, and either inadequate or excessive chemical dosage could result in poor SS removal. The optimal dosage for a specific coagulant was normally determined by jar tests. These tests had to be repeated when treatment conditions, such as the paint type and total solid loading, changed during the paint spray operation. In this study, a polymer coagulant (Betz Dearborn, Polymer D2611) currently used in an automotive assembly plant was compared with the EKF treatment. Jar tests were performed to obtain the optimal coagulant dosage. The procedure of jar tests was based on the description in the book titled *Wastewater Engineering: Treatment, Disposal, and Reuse* (Metcalf and Eddy 1991), and was confirmed with the chemical lab of the paint department in an automotive assembly plant.

A linear relationship between SS and turbidity was observed in this study. For other wastewater applications

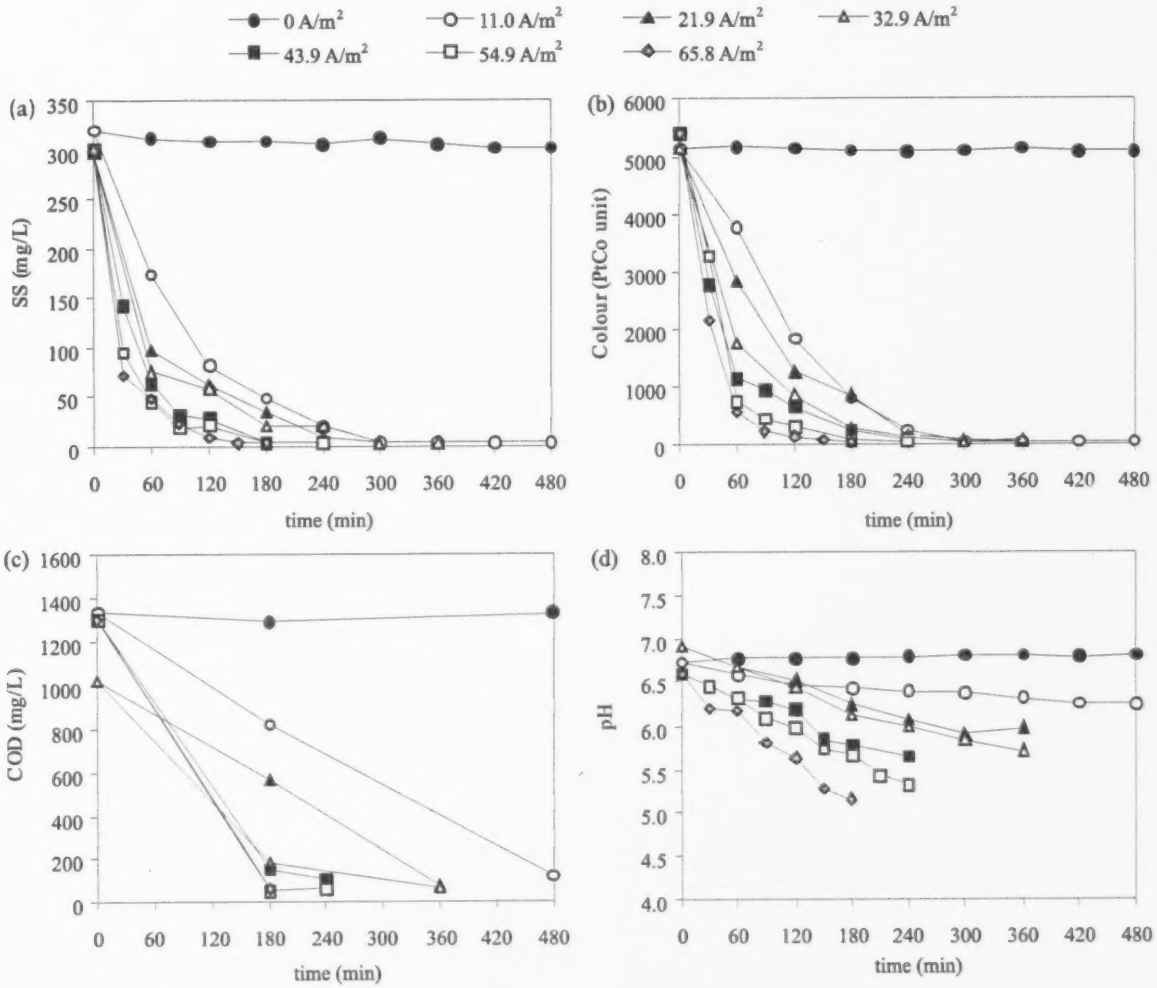

Fig. 3. Results of run W-B1 in water-borne base coat water (initial value: TS = 790 to 870 mg/L, SS = 296 to 320 mg/L).

(Metcalf and Eddy 1991; Xu et al. 2001), the linear relationship was also reported. Based on the above discussion, turbidity monitoring could be considered to indicate SS concentration.

Results and Discussion

Type and Initial Water Quality of Paint Water

Figure 3 shows the changes in SS, colour, COD, and pH versus flotation time for the water-borne base coat water sample (run W-B1). The trend was consistent for all three initial SS concentrations (see Table 3). The reduction of SS and colour was clearly shown in Fig. 3a and 3b, compared with the control test. The control test (i = 0 A/m^2) showed that concentrations of SS and colour were almost constant for 8 hours, indicating that the paint suspension was very stable. Quick decreases of both SS and colour concentrations were observed within the first 10 minutes by the EKF treatment, and higher current density caused faster effects. COD removal by the EKF is shown in Fig. 3c, and again, higher current density caused faster COD removal. The water pH decreased during the EKF tests, and again, a higher current density caused a faster and larger pH drop (Fig. 3d).

The paint particles were floated to the water surface as they were entrapped by oxygen (O_2) and hydrogen (H_2) gas bubbles generated from water electrolysis (Chen 2004). The total volume of H_2 and O_2 is a linear function of the applied DC current based on Faraday's law; a higher current generates larger H_2 and O_2 volume. In addition, the separation efficiency of a flotation process depends strongly on bubble sizes. The effective EKF obtained is primarily attributed to the generation of uniform and tiny bubbles (Chen 2004). Chen et al. (2002) reported that the sizes of the gas bubbles generated by water electrolysis were log-normally distributed, with over 90% of the bubbles in the size range of 15 to 45 μm. Dissolved air flotation produced typical gas bubble sizes ranging from 50 to 70 μm (Stevenson 1997), and electrostatic spraying of air produced gas bubbles ranging from 10 to 180 μm with a mean diameter of 33 to 41 μm (Tsouris et al. 1994). Therefore, a higher current generates more tiny bubbles, leading to better SS and colour removal.

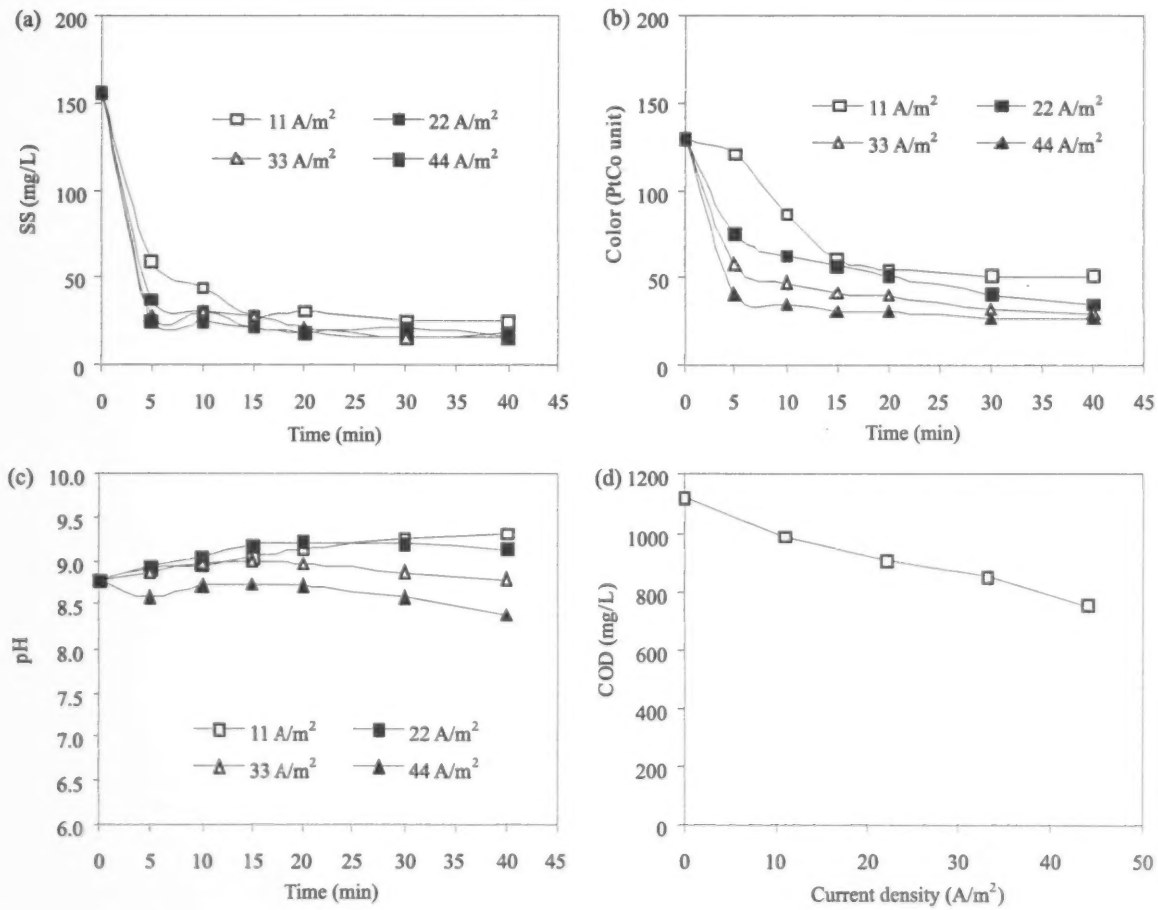

Fig. 4. Results of Run S-P1 in solvent-borne primer water (initial value: TS=1432.0 mg/L, SS=155.6 mg/L).

COD removal may be induced by electrooxidation of dissolved and colloidal organic components, and by flotation of microparticles and colloid components. Chen (2004) summarized the effects of organic compound removal in an electrokinetic process in an indirect electrooxidation process and direct anode oxidation. The indirect electrooxidation process uses the chlorine and hypochlorite generated anodically to destroy pollutants (Panizza and Cerisola 2006). Direct anodic oxidation occurs directly on the anodes by generating physically absorbed active oxygen to combust organic compounds into CO_2 or other oxidation products.

Water electrolysis generates equal amounts of hydroxide ion (OH^-) on the cathode and hydrogen ion (H^+) on the anode, as shown in following chemical equations:

$$\text{Cathode: } H_2O + 2e^- \rightarrow H_2\uparrow + 2OH^- \quad (3)$$

$$\text{Anode: } H_2O - 2e^- \rightarrow 1/2O_2\uparrow + 2H^+ \quad (4)$$

In other words, water electrolysis does not cause a change of pH in the water body. The pH decrease, as shown in Fig. 3d, may have been caused by the decomposition of organic compounds to low molecular-weight organic acids, as discussed above.

Typical results of the EKF tests on the solvent-borne paint water samples and mixed paint water samples are shown in Fig. 4 and 5, and include the water SS, pH, colour, and COD, as measured during runs S-P1 and M-M1. The experimental results demonstrate that the EKF process removed contaminants of SS and colour quickly from solvent-borne (see Fig. 4a and 4 b) and mixed paint water (see Fig. 5a and 5b). As shown in Fig. 4c and 5c, pH slightly increased and then dropped slowly. Higher current density caused a larger pH drop. The final COD concentrations after the 40 minutes EKF treatment (see Fig. 4d and 5d) indicate that COD removal increased linearly with increasing current density.

Based on the above experimental results, it can be concluded that the EKF process has significant paint/water separation effects on both water-borne and solvent-borne paints. Significant decolouration and COD removal were obtained simultaneously by the EKF process.

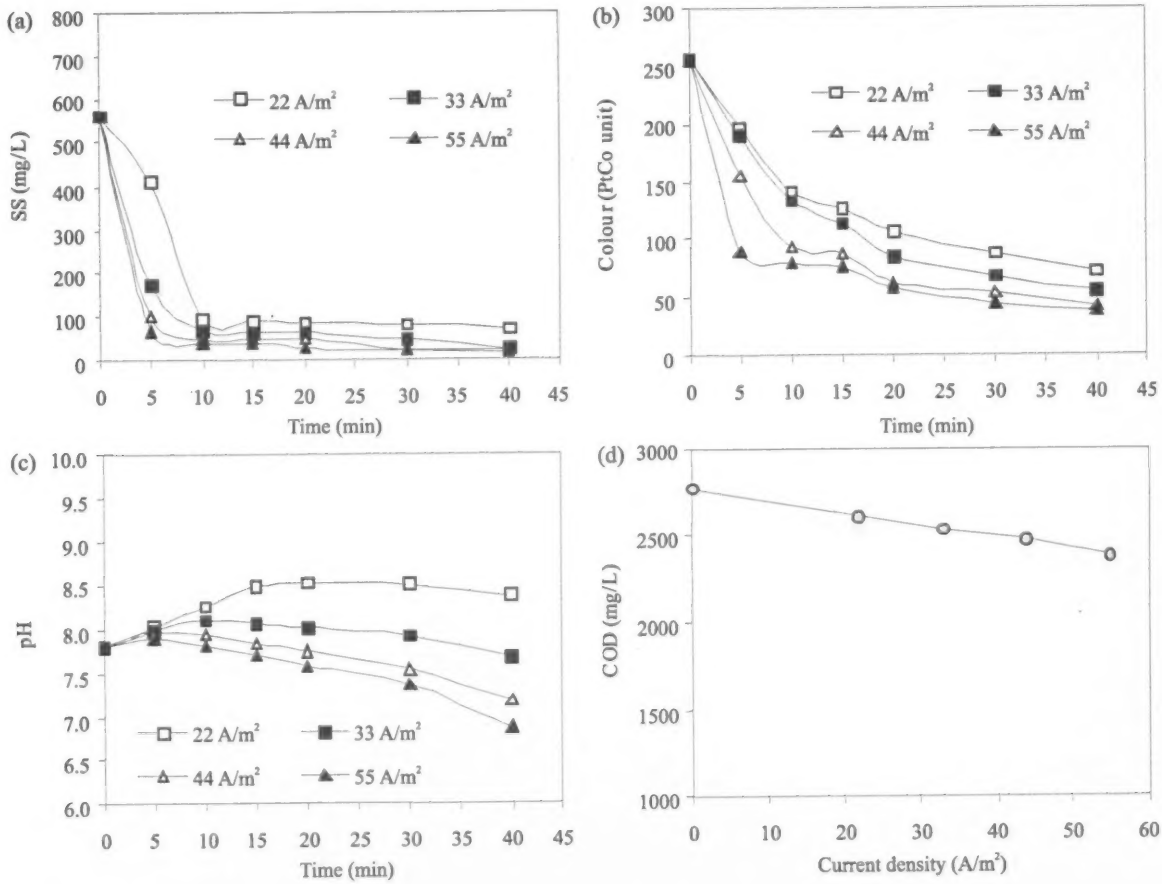

Fig. 5. Results of Run M-M1 in mixed paint water (initial value: TS=2789.0 mg/L, SS=562.4 mg/L).

Current Density

The percentage of SS removal, (η, see equation 2), time to reach a SS criterion, and concentration of floated sludge under various current densities were studied in this section. A SS concentration ≤100 mg/L was set as the SS criterion for water quality.

For the discussion of SS removal versus current density, experimental results from Fig. 3a, 4a, and 5a are represented in Fig. 6. The experimental results of all three types of paint water indicate that the SS removal rate increased with increasing current density, especially at the beginning period. At the current density of 43.9 A/m², the percentage of SS removal at 30 minutes for water-borne, solvent-borne, and mixed paint water were 52.7, 96.3, and 86.3%, respectively. The EKF process was more effective on the solvent-borne and mixed paint water samples than on water-borne paint water samples. The reason can be explained by the fact that the molecules of solvent-borne paint particles were hydrophobic, so they were immiscible with water but adsorbent with gas bubbles. On the other hand, the molecules of water-borne paint particles were hydrophilic, so they contacted the water at almost no contact angle, and as a result, it was difficult to adsorb to gas bubbles.

Figure 7 demonstrates the effects of applied current on flotation time, presented as the time to reach the SS criterion (SS ≤ 100 mg/L) versus the applied current density. The flotation time depended on the applied current density of the EKF process and the initial SS concentration of the paint water. Figures 7a and 7b show that the water-borne paint water samples needed more flotation time and/or current than solvent-borne and mixed paint water samples.

Figure 8 presents the solid content of the floated sludge collected from the EKF CEll after 40 minutes of flotation operation. The solid content was defined as the percentage of dry solid per wet sample. The solid content of the floated sludge slightly increased with increasing applied current density in all paint water samples. The solid content of the floated sludge also increased with the increase of initial SS concentration (see fig. 8a and

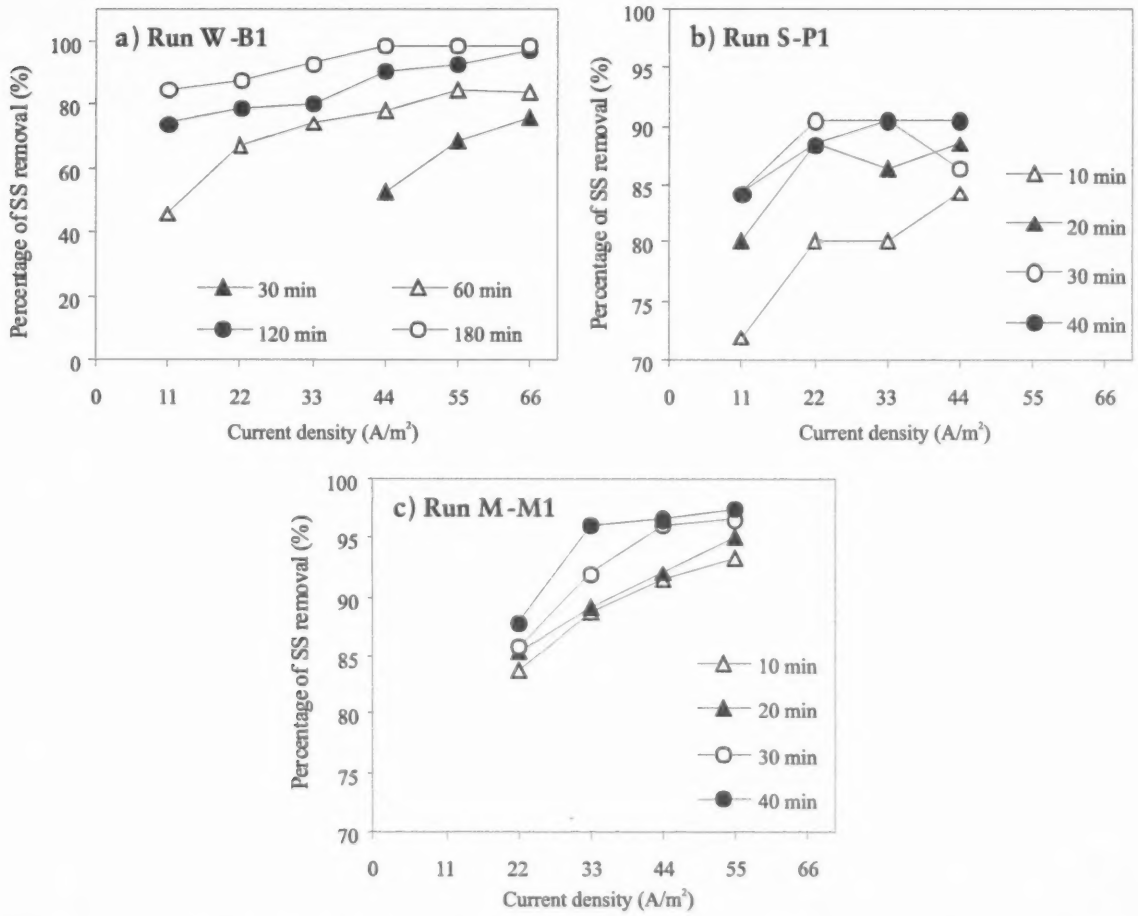

Fig. 6. Percentage of SS removal (η) by the EKF process as a function of current density on water-borne paint water (W-B1), solvent-borne paint water (S-P1) ,and mixed paint water (M-M1).

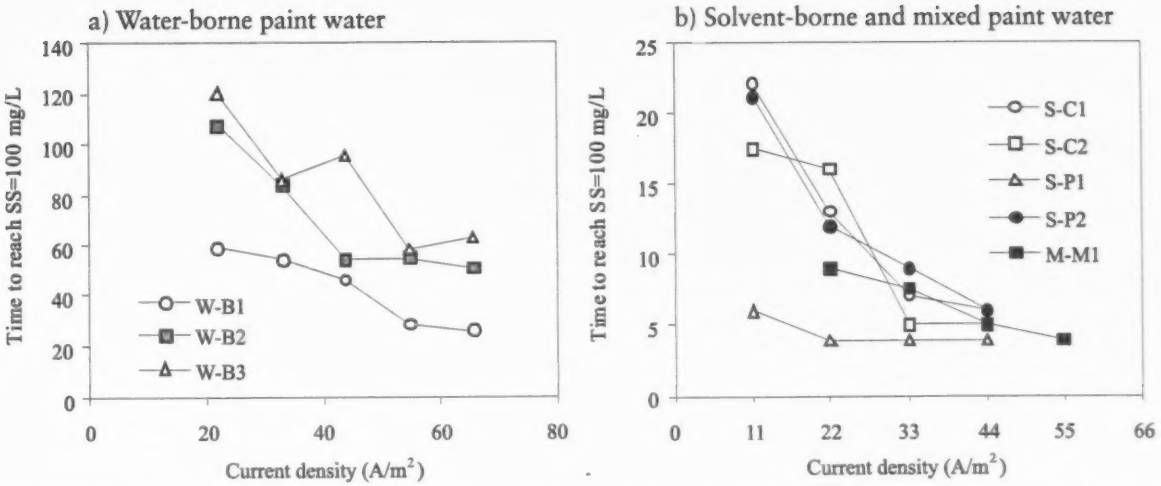

Fig. 7. Applied current density versus operating time until the remaining suspended solids reach a SS criterion of ≤100 mg/L.

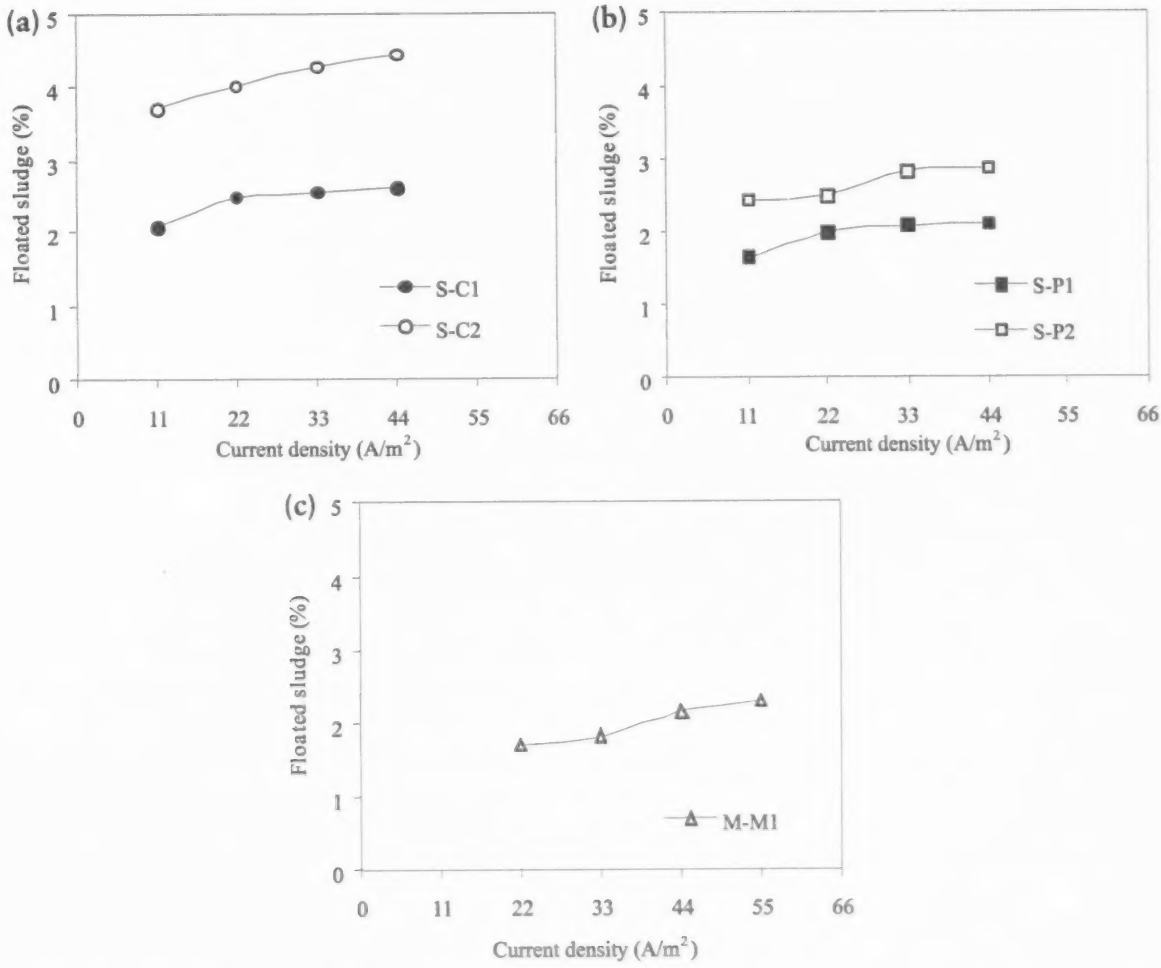

Fig. 8. Solid content of floated paint sludge after the EKF treatment (floatation time was 40 minutes for each experiment).

8b). This may be due to the fact that the pore water was squeezed out of the floated sludge layer in the flotation cell by vertical forces of the gas bubbles' buoyancy and the sludge's self-weight. The higher applied current density generated more gas bubbles which caused higher buoyancy, and the greater thickness of the sludge layer caused a higher self-weight. As a result, much more pore water could be squeezed out from the floated sludge.

Comparison of Electrokinetic Flotation and Chemical Coagulation

The jar test results on solvent-borne paint sludge water are shown in Fig. 9a in comparison with those from the EKF treatment (run S-C2), as shown in Fig. 9b. The jar test showed that the coagulant reduced the turbidity in the paint water and that there was an optimum coagulant dosage of 3 mg/L, at which the turbidity of the paint water was lower than 10 FTU. The turbidity increased with increasing dosage, indicating the chemical treatment should be closely monitored in order to keep optimum dosage with the various initial SS concentrations. Chemical coagulants may generate several effects (e.g., the double layer compression, adsorption charge neutralization, sweep floc formation, and adsorption-inter-particle bridging [Droste 1997]). The required dosage for a chemical treatment is related to the amount of suspended solids and type of particles to be removed, as well as the degree of anionic surface charge which must be neutralized. The optimum coagulant dosage will neutralize the surface charge on the particles, allowing coagulation to take place. However, an excess of coagulant will replace the anionic surface charge with a cationic charge and can redisperse the solids, resulting in poor turbidity removal. Coagulant demand will vary from water source to water source, so it is not feasible to provide generalized guidelines on coagulant dosage versus influent SS concentration. In addition, it was observed that in all jar tests, the paint sludge settled instead of floated after the coagulant dosage. Therefore, additional measures must be taken to generate sludge flotation in the paint water treatment process, such as supplying air bubbles into the water body. On the other hand, the EKF treatment could reduce the turbidity to the same level in five minutes as the chemical treatment at optimum coagulant dosage. The turbidity removal effect was slightly improved by extended flotation time.

Chemical coagulation has limitations such as high costs for chemicals, handling, and sludge disposal of chemicals. It also frequently encounters operation problems (Metcalf and Eddy 1991). The paint sludge generated from chemical coagulation can be difficult to dewater because almost all coagulants, such as alum salt, iron salt and polymer combine with water molecules and increase the volume of the sludge. On the other hand, the floated sludge from the EKF process does not include a polymer coagulant, and the moisture generally stays in the sludge pores by free-water molecules instead of polymer-combined water molecules in chemical coagulation. As a result, sludge from the EKF process can be more readily dewatered by squeezing, heating, etc. Another added advantage of the EKF process is that because chemical usage is reduced, the paint sludge will have a lower volume and be more readily dewatered. Based on the above discussion, it can be concluded that the EKF process can achieve similar turbidity removal results compared with the chemical coagulation process when the EKF operational time is in the range of 5 to 40 minutes.

The operational robustness of the EKF process for achieving a SS criterion is discussed using Fig. 7 and 9. Figure 7 shows that the SS criterion of ≤100 mg/L was achieved by adjusting either flotation time or current density. Both operations were easily implemented. The robustness can also be seen in Fig. 9b, where turbidity declined to 10 FTU at 5 minutes, and over flotation did

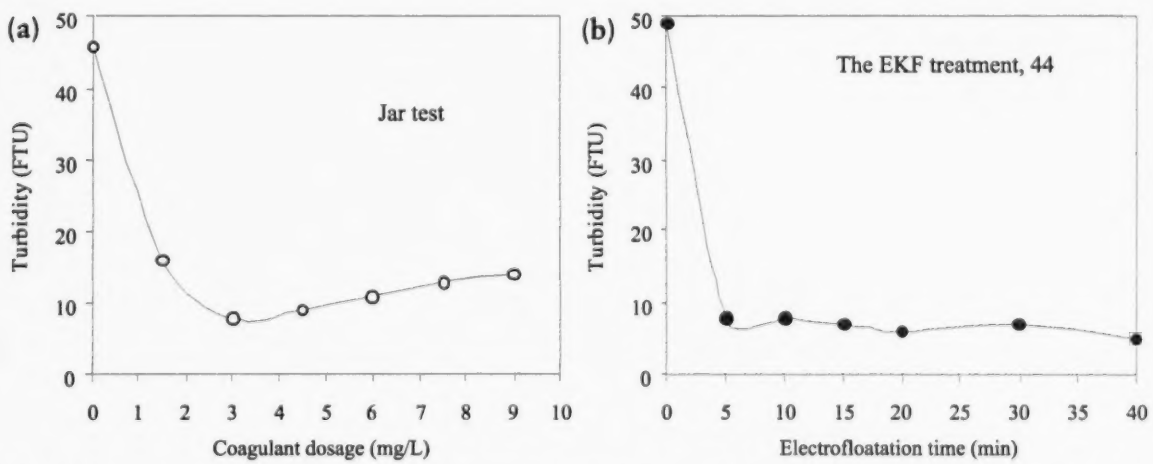

Fig. 9. Comparison of chemical jar test and the EKF for turbidity removal in solvent-borne paint water (initial value: TS = 4600.0 mg/L for jar tests, and TS=4669.3 mg/L for the EKF).

not cause turbidity to increase as it did in the chemical coagulation process (see Fig. 9a).

Conclusions

The conclusions from this work are:

- The EKF process generated quick flotation of suspended paint particles without adding any coagulant. The concentrations of SS in the paint water samples were significantly reduced with colour and COD removal obtained simultaneously.
- The EKF process removed contaminants of SS and colour quicker from solvent-borne paint water than from water-borne paint water.
- Paint type, initial SS, and current are the most important parameters for the EKF process. While for a given paint water, applied current and flotation time are major parameters for controlling water quality and energy consumption. Other parameters governing the effectiveness of solid/water separation, treatment time, and power consumption include water pH, electrode-module design, electrode material, particle size, and particle zeta potential.
- The EKF process has shown great potential for replacing coagulants and other chemicals in the treatment of process water from paint spray booths.

Acknowledgments

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